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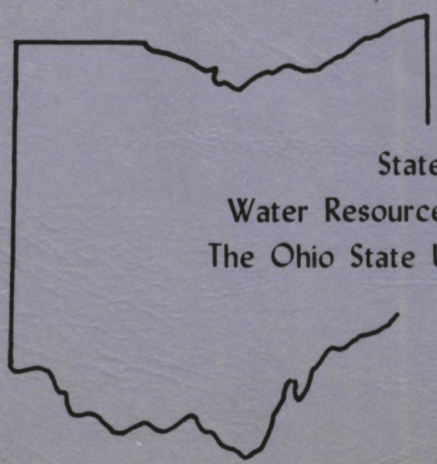

State of Ohio
Water Resources Center
The Ohio State University

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by

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ABSTRACT

Groundwaters in the Northwest School System area of Canal Fulton, Ohio were examined for their hydrologic and chemical properties. In general, the groundwaters in the study area were inter-connected by a complex system of aquifer and aquitards. Arsenic concentrations were above EPA limits in two wells, but were elevated above the background value throughout much of the area.

Two major aquifer systems exist within the study area: The Sharon Sandstone of the upland areas; and the outwash sand and gravel deposits of the buried valleys. Flow is generally from the north, but local variations are caused by the Tuscarawas River Valley on the south and west of the study area. Recharge to the local aquifer system may be occurring in the central portion of the study area from the chloride-contaminated Tuscarawas River. The areal distribution of arsenic within the study area indicates that the arsenic is not sourced from the Tuscarawas River and gives no indication of an outside source of arsenic.

Within the study area, there is no evidence for an anthropogenic source of arsenic to the groundwaters. Agricultural soils, abandoned underground coal mines, industrial impoundments to the north, and an abandoned industrial dump site within the study area were all eliminated as possible sources for the arsenic. Theoretical and laboratory studies of arsenic in these groundwaters demonstrates that it is entirely of inorganic make-up, and consists of about equal parts of arsenate and arsenite. Redox considerations suggest that arsenic is controlled by an adsorption equilibrium with ferric hydroxides, and that the reduction of the ferric hydroxides by a recent lowering of Eh and/or pH in the aquifer has liberated both iron and arsenic to solution. A high

correlation between ferrous iron and total dissolved arsenic supports this model.

ACKNOWLEDGEMENTS

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The assistance of Mr. C.M. Oatley, Superintendent and Mr. M. Dagger, Chief Custodian of the Northwest Local School System in Canal Fulton is gratefully appreciated. Dr. W.H. Strain, Cleveland Metropolitan General Hospital assisted in the public health aspects of the study. Dr. A.W. Varnes, SOHIO Research, donated his expertise, staff, and equipment to assist in the arsenic analyses.

CONTENTS

FIGURES

TABLES

BACKGROUND

In July of 1978, a routine water sample was collected by the Ohio Environmental Protection Agency for a new well at the Stinson Elementary school near Canal Fulton, Ohio. Analysis of this water sample indicated that arsenic levels exceeded the drinking water standard of 50 ug/l. Nearby wells of the Northwest Intermediate School and the Northwest High School were subsequently sampled. The well of the intermediate school was found to exceed permissible levels, and the high school well contained above background but permissible levels of arsenic. The contaminated wells were removed from service by order of the Ohio E.P.A. Sampling of well water at nearby residences uncovered arsenic levels above ambient background levels but within the safety limits of the drinking water standards.

There are no previously reported cases in Ohio of arsenic contamination of ground water resources. Ohio is heavily reliant upon its safe and abundant supply of ground water (serving one half of the population). This unsafe and unusual condition, therefore, warranted further study.

CONCLUSIONS AND RECOMMENDATIONS

Eighty-eight water wells were sampled in the study area to determine the areal extent of arsenic contamination, to evaluate the hydrogeology, and to permit an assessment of the likelihood of recurrence of the contamination and the possibility of a similar problem occurring elsewhere.

Elevated and non-permissible levels of arsenic were discovered in two water wells. Elevated but permissible levels were found in eleven wells, and many other wells had arsenic concentrations above the regional background value. The areal distribution of the arsenic concentrations and the hydrogeology of the study area rule out the possibilities that the arsenic is being transported into the study area or that it is of anthropogenic origin.

Adsorption of arsenic to ferric oxyhydroxides in the rock aquifer is suggested as the controlling mechanism for arsenic in these ground waters. Under oxidizing and neutral or mildly basic conditions ferric oxyhydroxides are stable. Minor decreases in Eh or pH can result in the dissolution of the solid and the liberation of ferrous iron and arsenic to the ground water. Such a process may have occurred recently in the study area, resulting in the observed high levels of dissolved arsenic and ferrous iron.

The possibility exists for this process to occur elsewhere in Ohio. However, the specific conditions including redox, pH, mineralogy, and the necessary sequence of changes within the hydrogeochemical system that produced this contamination, is not likely to be repeated on a wide scale or result in high concentrations of arsenic. In addition, it is reasonable that once the liberated arsenic is discharged, the water quality will improve. Depending upon the location, this could be several years, or several centuries.

Alternative water supplies include the drilling of new wells to different aquifers or removal of the arsenic. Ten methods of arsenic removal

from drinking water supplies have been reported by Ferguson and Anderson (1974). One of the more promising methods is the adsorption of arsenate and arsenite onto amorphous ferric and aluminum hydroxides. Equilibrium adsorption experiments by these workers demonstrate the hydrous oxide adsorption of both arsenate and arsenite. Removal of sufficient amounts of arsenic to meet drinking water standards through hydrous oxide adsorption has been reported by Irukayama (1964). Buswell et al. (1943), however, has reported the failure of this process. Ferguson and Anderson (1974) suggest that occlusion or precipitation may also be involved where this method has produced the desired results.

Household plumbing systems can increase arsenic concentrations in drinking waters to above the 50 ppb EPA limit. Flushing the household system of standing water before use should reduce the arsenic, lead, and other toxic metal concentrations in the drinking water in these cases.

INTRODUCTION

Arsenic in drinking water, when present in excess of 50 ppb, is considered a hazard to human health. Both the U.S. E.P.A. and the World Health Organization have adopted this standard. In Antofagasta, Chile, a public water supply containing 800 ppb of arsenic resulted in many health conditions related to arsenicism (Borgono et al., 1976). Concentrations of arsenic in artesian wells in Taiwan that varied from 0.4 to 0.6 ppm resulted in many cases of hyperpigmentation, keratosis, and peripheral vascular disorders (Tseng et al., 1968). Both chronic and acute arsenic poisining have been reported, and recent evidence has indicated a possible link between arsenic andskin cancer (Wagner et al., 1979; Tseng et al., 1968). A recent compilation of the medical effects of arsenic on human health is given by the National Research Council (1977).

Arsenic, a naturally occurring element, is widely distributed in the global environment. It is twentieth in abundance among the elements that make up the earth's crust (Onishi, 1969). Ore minerals of arsenic include arsenic metal (As), arsenopyrite (FeAsS), realgar (AsS), and orpiment (As_2S_3), and arsenic has been identified in many other minerals. Both sedimentary iron ores (oxides) and coal may contain as much as 2000 ppm arsenic (Onishi, 1969). The concentration of arsenic in most sedimentary pyrite ranges from 600 to 900 ppm and a value of 7,800 ppm has been reported in a marcasite sample. Of six sample analyses reported by Fleischer (1955) only one was above 1000 ppm (7,800 ppm), two were between 500 and 1000 ppm and three were less than 500 ppm.

Anthropogenic contributions of arsenic to the environment include: insecticides; herbicides, crop dessicants, wood preservatives; feed additives; pharmaceuticals; war gasses; riot control agents; and metallurgical additives.

The burning of coal results in a condition or arsenic fallout (National Academy of Sciences, 1977). The inorganic forms of arsenic found in natural waters are: arsenic acid (H_3AsO_4); arsenious acid (H_3AsO_3); arsenic sulfide ($HAsS_2$); arsenic metal (As); and arsine gas (AsH_3). The oxidation states of these species are +5, +3, +3, 0, and -3 respectively (Ferguson and Gavis, 1972). The soluble organic forms of arsenic that are typical to natural waters are: monomethyl arsonic acid ($CH_3AsO(OH)_2$) (abbreviated as MMA); dimethyl arsinic acid ($(CH_3)_2AsOOH$) (abbreviated as DMMA); dimethyl arsine ($(CH_3)_2AsH$); and trimethyl arsine ($(CH_3)_3As$). Oxidation states are +3, +1, -3, -3, respectively (Holm et al., 1979).

Transformation of the arsenic species from inorganic to organic is a result of biomethylation. The biomethylation of arsenate occurs as a series of reductions. McBride and Wolfe (1971) have concluded that within the methanobacterium the following sequence of reactions occurs: arsenate (+5) is reduced to arsenite (+3); arsenite is methylated to monomethyl arsonic acid (+3); monomethyl arsonic acid is reduced and methylated to dimethyl arsinic acid (+1); dimethyl arsinic acid is reduced to dimethylarsine (-3). All intermediates will also be converted to dimethylarsine.

Woolson and Kearney (1973) demonstrated the conversion of dimethyl arsinic acid to a methylated arsine (presumably dimethylarsine) under both anaerobic and aerobic conditions. Arsenate was also a product under aerobic conditions. Arsenite and a nutrient media were added to a sample of pond water by Braman (1975). Production of alkyl-arsenic acids and trimethyl-arsine was observed in this aerobic environment. Since methanobacterium is is an anaerobic organism (McBride and Wolfe, 1971), Braman (1975) concluded that this organism is not the sole source of environmental biomethylation.

Dimethylarsine is unstable under oxidizing conditions and may undergo

conversion to dimethyl arsinic acid which in turn may be metabolized to arsenate (Woolson and Kearney, 1973).

Pierce and Moore (1980) demonstrated the adsorption of arsenite onto amorphous iron hydroxide ($Fe(OH)_3$). The adsorption of arsenate onto amorphous aluminum hydroxide has been studied by Anderson, Ferguson, and Gavis (1975), and by Malotky and Anderson (1976). These adsorption reactions are cited by Holm et al. (1979) as having an effect on the transport of arsenic and apparent species transformation rates in heterogeneous aquatic environments. Since most natural aquatic environments are heterogeneous, that is, containing both solid and dissolved phases, Holm et al. (1979) concludes that the role of adsorption in controlling total dissolved arsenic is important.

The primary objective of this study is to identify the source of the arsenic in some Ohio ground waters and evaluate the possibility of a similar problem occurring elsewhere. From the above earlier studies it is apparent that the fate and potential health hazard of arsenic in natural waters is dependent upon the redox conditions of the environment and mineralogical controls of arsenic. The approach utilized in this study is to determine the chemical speciation of the arsenic, determine the transporting mechanism (dissolved, complexes, adsorbed onto particles, etc.), and identify the direction of ground water flow within the contaminated aquifer. These results will not only permit an assessment of the objectives of this study, but will provide general information on the behavior of arsenic in the environment.

ARSENIC GEOCHEMISTRY

The chemistry of arsenic in natural aquatic systems is complex, but predictable. The soluble arsenic species that exist within a given natural water system are controlled by a combination of redox conditions, adsorption reactions, precipitation of solid arsenic phases, and microbial transformations. Each of these mechanisms and several in combination will influence and potentially control the mobility of arsenic within a given aquatic environment. Arsenic may be transmitted, accumulated, stored, and released according to variations in environmental controls.

There are five stable oxidation states of arsenic: +5, +3, +1, 0, -3 (Holm, 1979). In natural waters, the toxicity of arsenic compounds varies with the arsenic oxidation state. Soluble compounds having an oxidation state of +5 are the least toxic and those having the +3 oxidation state are the most toxic (Ferguson and Gavis, 1972).

The soluble arsenic species that are found in natural waters are listed in Table 1. The solid species realgar (AsS) (a covalent compound (Ferguson and Anderson, 1974)) and orpiment (AsS_3), are included in systems containing sulfur (Ferguson and Gavis, 1972; Wagemann, 1978).

Other solid species including ferrous arsenate (Ferguson and Gavis, 1972; Wagemann, 1978), barium arsenate ($BaAsO_4$), and chromic arsenate ($CrAsO_4$) are possible controls for arsenic solubility (Wagemann, 1978). The gas phase (-3) arsine (AsH_3) is a species that is stable at very low Eh conditions only.

The Gibbs Free Energies (ΔG_f°) of the arsenic species at standard conditions (25°C and one atmosphere) have been critically compiled for internal consistency, and are listed in Table 2. An Eh-pH diagram for an aquatic system at standard conditions with total arsenic $10^{-5.63}$ mol l^{-1},

Table 1. Arsenic species commonly found in natural waters.

Species	Name	Oxidation State
H_3AsO_4	Arsenic Acid	+5
$H_2AsO_4^{-1}$		
$HAsO_4^{-2}$		
AsO_4^{-3}		
H_3AsO_3	Arsenious Acid	+3
$H_2AsO_3^{-1}$		
$HAsO_3^{-2}$		
$HAsS_2$		+3
AsS_2^-		
$CH_3AsO(OH)_2$	Monomethyl Arsonic Acid	+3
$(CH_3)_2AsOOH$	Dimethyl Arsinic Acid	+1
AsH_3	Arsine (gaseous)	-3
$(CH_3)_2AsH$	Dimethyl Arsine (gaseous)	-3
$(CH_3)_3As$	Trimethyl Arsine (gaseous)	-3

Table 2. Selected Gibbs Free Energy values for arsenic compounds.

Species	State	ΔG_f°(KCal/mole)	Reference*
H_3AsO_4	aq	-183.1	1
$H_2AsO_4^{-1}$	aq	-180.04	1
$HAsO_4^{-2}$	aq	-170.82	1
AsO_4^{-3}	aq	-155.00	1
H_3AsO_3	aq	-152.94	1
$H_2AsO_3^{-1}$	aq	-140.35	1
$HAsO_3^{-2}$	aq	-125.3	2
$HAsO_2$	aq	- 96.25	1
AsO^{+1}	aq	- 39.15	1
AsO_2^{-1}	aq	- 83.66	1
As_2O_5	c	-187.0	1
As_4O_6	c	-275.46	1
AsH_3	g	+ 16.47	1
AsN	g	+ 40.15	1
NH_4AsO_2	aq	-102.63	1
$NH_4H_2AsO_3$	aq	-159.32	1
$NH_4H_2AsO_4$	c	-199.1	1
$NH_4H_2AsO_4$	aq	-199.01	1
$(NH_4)_2\ HAsO_4$	aq	-208.7	1
$(NH_4)_3\ AsO_4$	aq	-211.91	1
AsS	c	- 16.81	3
As_2S_3	c	- 40.3	1
FeAsS	c	- 12.0	4
$HAsS_2$	aq	- 16.25	5
AsS_2^-	aq	- 11.2	6
$FeAsO_4$	c	-183.71	6

*1 Wagman et al. (1968)
2 Sergeyva and Khodakovskiy (1969)
3 Robie and Waldbaum (1968)
4 Wagman et al. (1969)
5 Sillen and Martell (1964)
6 Sillen and Martell (1971)

total sulfur $10^{-5.63}$mol l^{-1}, (total barium $10^{-5.63}$mol l^{-1}) is constructed from this data and is shown in Figure 1. Each arsenic species is predominant within given regions subject to controls of Eh, pH, total arsenic and total sulfur. Arsenic acid predominates within relatively high Eh regions, and arsenious acid predominates under less oxidizing conditions. Both of these polypotic acids respond to increases or decreases in pH by respective proton loss or gain. Soluble and solid arsenic sulfide compounds are stable at moderately low Eh. The soluble species are $HAsS_2$ and AsS_2^-, the solid species are realgar (AsS) and orpiment (As_2S_3). Metallic arsenic (As) predominates only under maximum reducing conditions in natural waters.

For a given oxidation state of arsenic, the distribution and predominence of each species is a function of the pH and the concentrations of all complexing species. The concentrations used in the calculations are: total arsenic = $10^{-5.63}$moles/liter; total sulfur = 10^{-6}moles/liter; and total ammonium = 10^{-1}moles/liter. The results of the calculations are illustrated in Figures 2 and 3 for the +5 oxidation state and in Figures 4 and 5 for the +3 oxidation state. Figure 2 is a system containing only arsinic acid. The distribution of progressively deprotinated species is uniform and without interference. Figure 3 is the same arsinic acid system, with the addition of the ammonium ion (10^{-1}M l^{-1}). This high concentration of ammonium resulted in the ammonium arsenate complex comprising 9 percent of total arsenic from pH 4.4 to 4.6. This ion pair represented less than 1 percent of total arsenic below pH 1.3 and above pH 7.7. Substitutions of lower ammonium concentrations, representing typical natural conditions ($NH_4^+ = 10^{-3.85}$M l^{-1}), yielded less than significant amounts of ammonium arsenate complex.

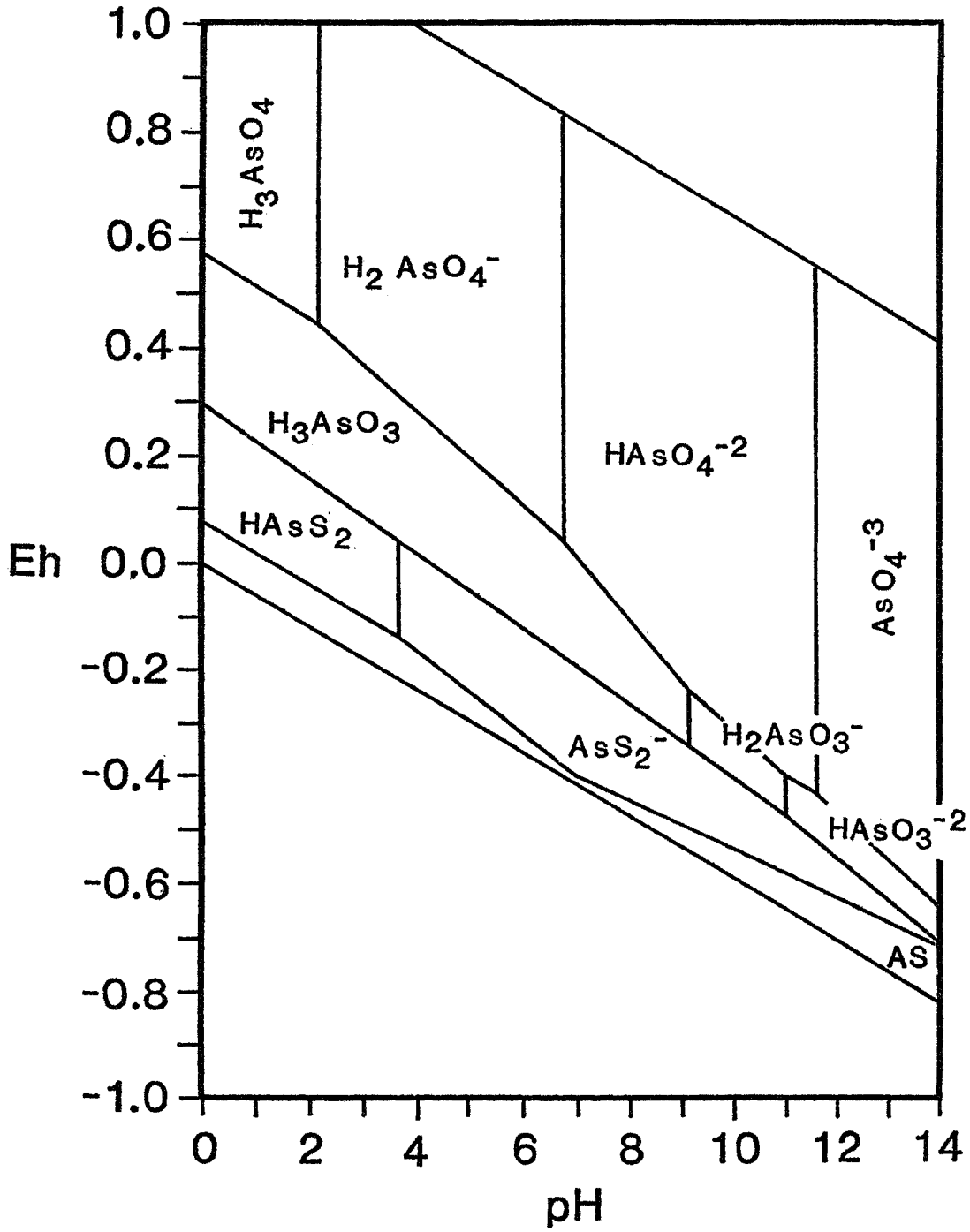

Figure 1. Eh-pH diagram for arsenic at 25°C and one atmosphere with total arsenic $10^{-6.174}$ mol l^{-1} and total sulfur 10^{-6} mol l^{-1}.

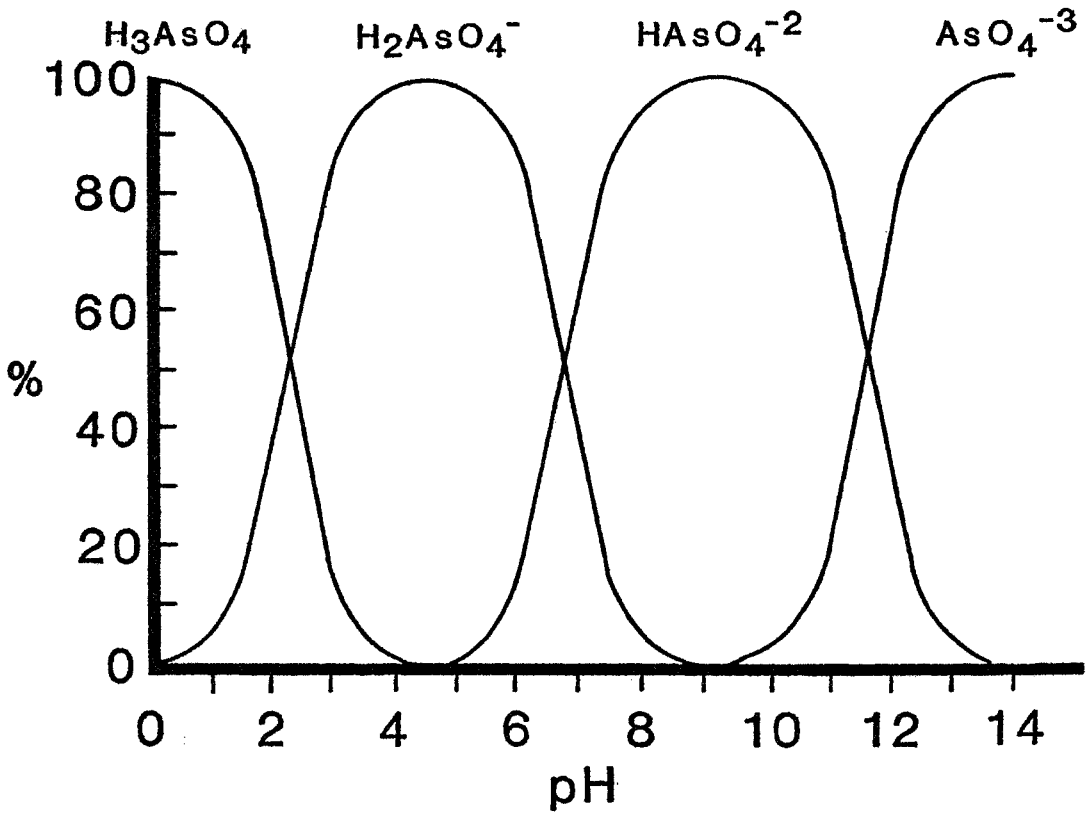

Figure 2. Species distribution diagram at 25°C and one atmosphere for arsenate.

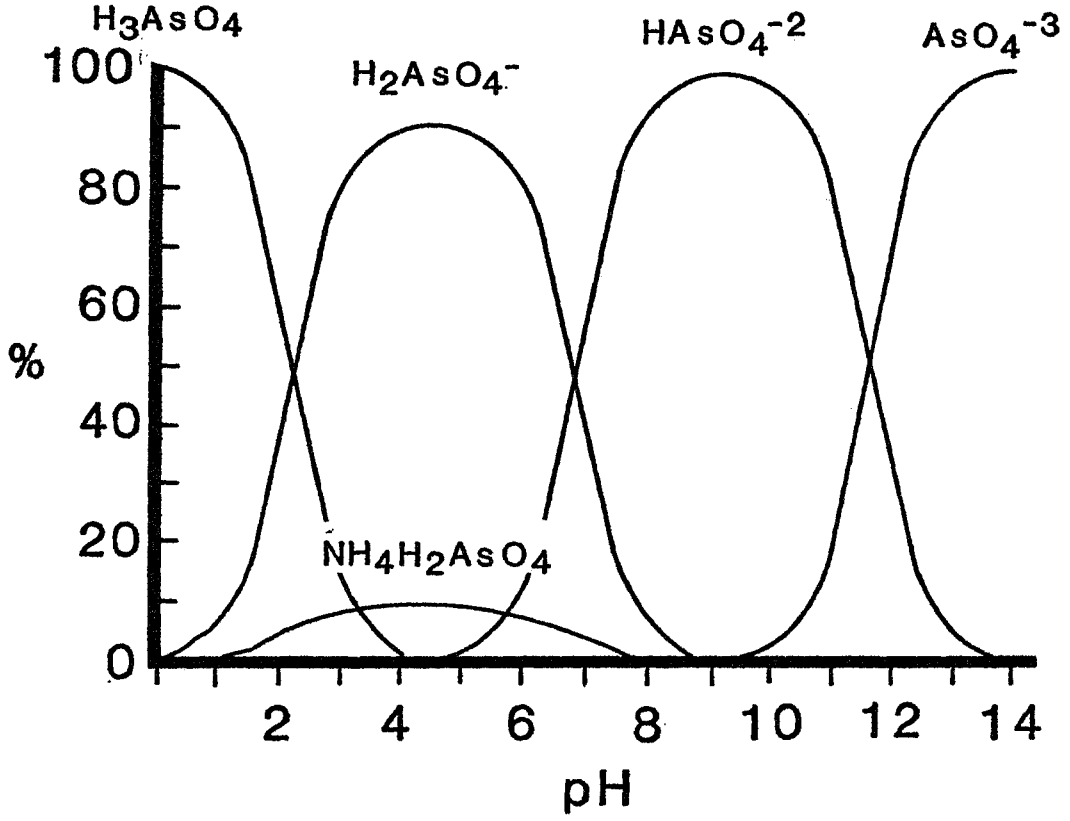

Figure 3. Species distribution diagram at 25°C and one atmosphere for arsenate and ammonia. Total arsenic = $10^{-5.63}$ mol l^{-1} and total ammonium = 10^{-1} mol l^{-1}.

Figure 4 illustrates the distribution for the arsenic (+3) species. Included in the system are arsenious acid and the soluble arsinic sulfides. This system was fixed with total arsenic equal to $10^{-5.63}$ mole liter^{-1}, total sulfur equal to $10^{-6.0}$ mole liter^{-1}, and total ammonium equal to $10^{-3.85}$ mole liter^{-1}. The calculation indicates predominance of the soluble arsenic sulfide species. AsS_2^- is then clearly indicated as predominant under reducing conditions and at pH typical to most natural waters.

The specific effects of Eh and pH conditions on arsenic mobility have been discussed by Gulens, Champ, and Jackson (1979). The formation of arsenic iron complexes as these environmental conditions are varied was investigated with elution studies through sand columns (sand grains having hydrous oxide surfaces). The results of their work show a marked distinction in mobility of arsenic (V) and arsenic (III) as the Eh-pH conditions are varied. Ground water environments are divided into three Eh-pH classes: oxidizing with pH = 5.7; neutral with pH = 6.9; and reducing with pH = 8.3. Under acid oxidizing and neutral Eh-pH conditions, arsenic III mobility significantly exceeds that of arsenic V. Both species are highly mobile under basic reducing conditions. All elutions were run with waters low in sulfide and thus the formation of arsenic sulfide precipitates was not considered. This study did not vary pH within each redox category, as each category was maintained at fixed pH by buffering. The authors point out that control of mobility may be related to both Eh and pH variation.

Arsenic speciation for the ground water of this study was determined using two analytical procedures. The chromatographic method of Yamamoto (1975), as modified by Holm and others (1979), was used to identify the arsenic species as inorganic or organic. Polarographic methods (Henry

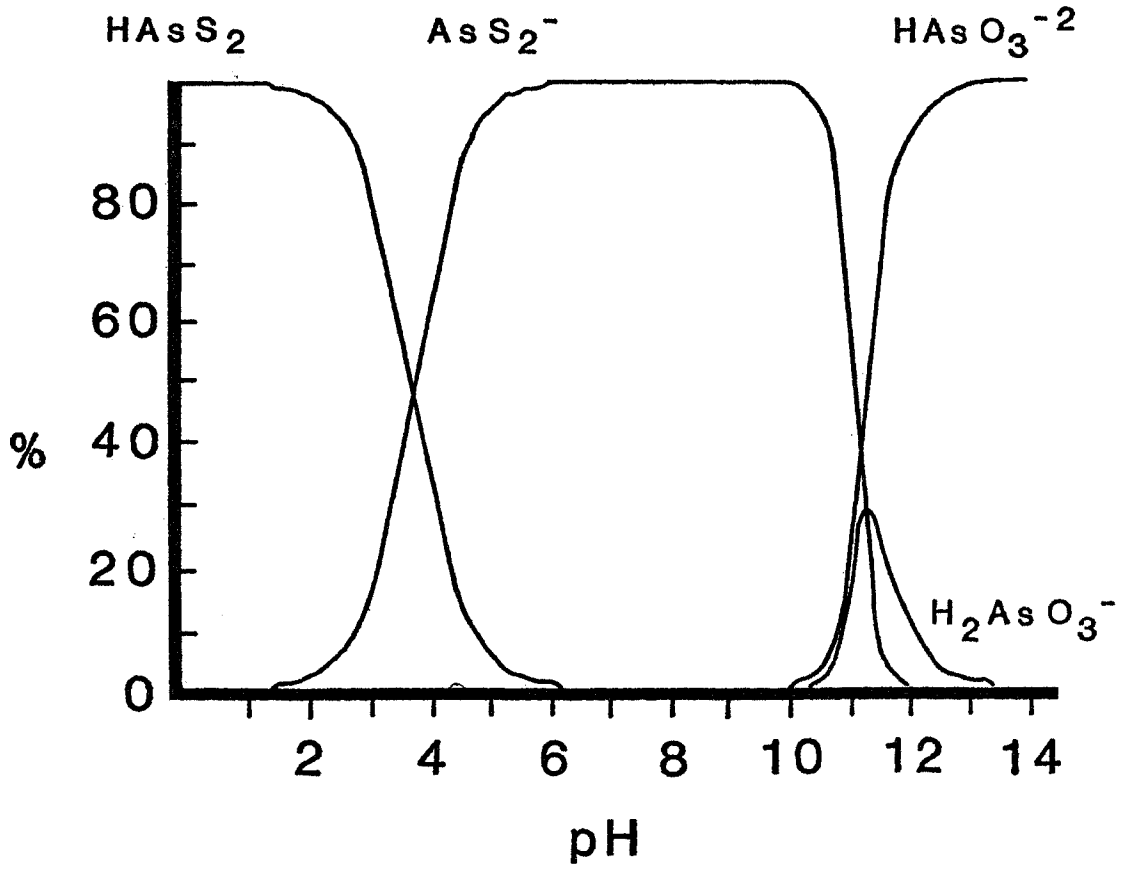

Figure 4. Species distribution diagram at 25°C and one atmosphere for arsenite and sulfur. Total arsenic = $10^{-5.63}$mol l^{-1} and total sulfur = 10^{-6}mol l^{-1}.

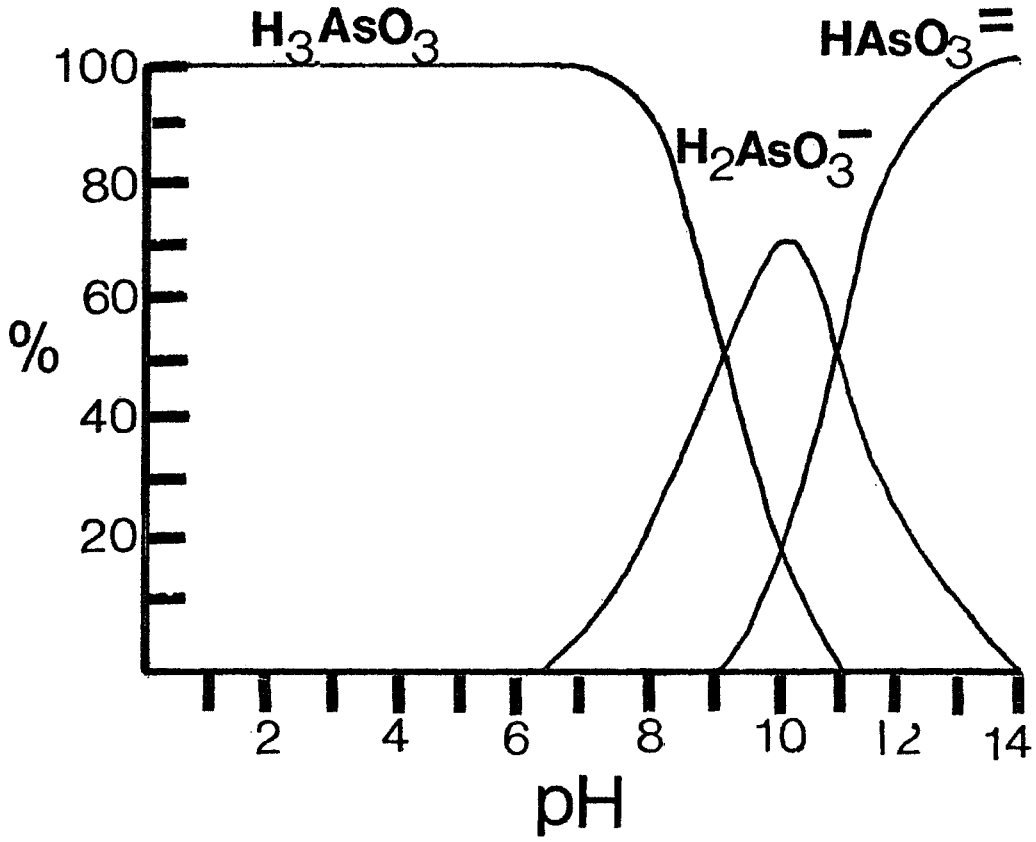

Figure 5. Species distribution diagram at 25°C and one atmosphere for arsenite.

and others, 1979) were then used to determine species oxidation state. The chromatogram of a sample collected from the Northwest Intermediate School (Figure 11) indicates the presence of inorganic arsenic only. The sample was analyzed polarographically for arsenic III (arsenic V is electroinactive). The concentration of arsenic III for this sample was 50 ug l^{-1}. Measurement of total arsenic for another sample collected from well yielded a value of 96 ug l^{-1}. We can then estimate that 52 percent of the total dissolved arsenic is arsenic III and 48 percent is arsenic V. Determination of ground water redox conditions by analyzing for specific arsenic species is discussed by Cherry et al. (1979). Eh can be estimated if pH is known and the ratio of arsenic III and arsenic V is determined. The "redox window", as defined by these authors, refers to an Eh range where both species are detected. Assuming the nearly equal concentration of eaeh species, the Eh conditions of this ground water (which is at pH 7) is readily determined from the Eh diagram (Figure 6). The Eh boundary between arsenate predominance and arsenite predominance represents, at any given pH, equal concentrations of each species. At pH = 7, this boundary coincides with Eh = 0.016 volts.

The stability of iron solids in the given context of Eh = 0.016 volts and pH = 7, where total dissolved iron equals 1.4×10^{-4} moles per liter, is also considered. Utilizing the Eh-pH diagram (Figure 1) these Eh-pH coordinates for the given concentration, when considered with respect to $Fe(OH)_3$, indicate a boundary or near boundary condition between Fe^{+2} and $Fe(OH)_3$. This suggests that if arsenic is controlled by an adsorption equilibrium with ferric hydroxides, then the reduction of ferric hydroxides should liberate both iron and arsenic to solution. Thus, ferrous iron and total dissolved inorganic arsenic should be directly correlated.

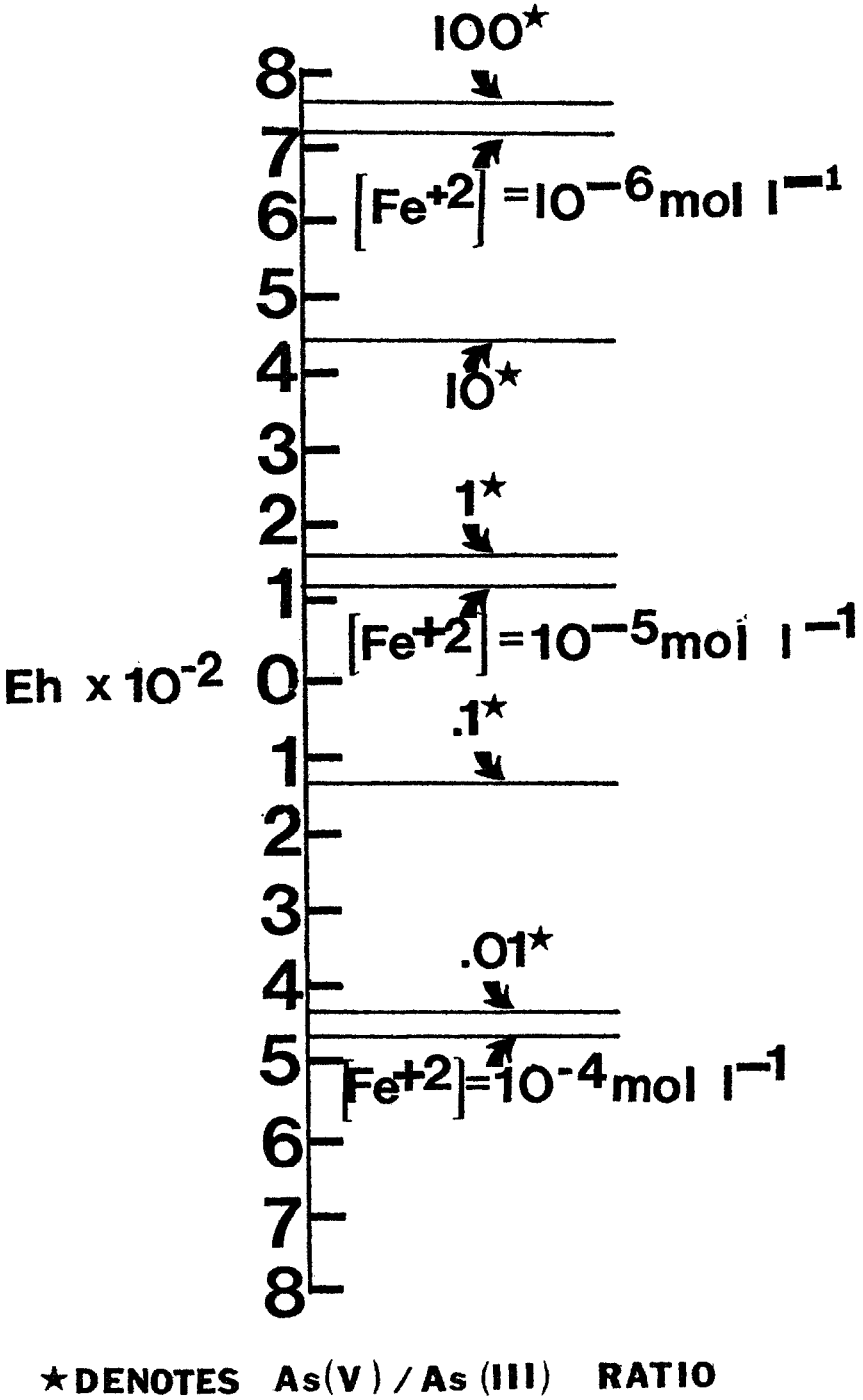

Figure 6. Expanded scale Eh stability diagram at pH 7, 25°C, and one atmosphere for arsenic and iron. Total arsenic $10^{-5.63}$mol l^{-1} and total iron 10^{-1}mol l^{-1}.

Removal of arsenic from solution by adsorption and surface precipitation is discussed by Ferguson and Anderson (1974), Anderson, Ferguson and Gavis (1975), and Holm and others (1979). Ferguson and Anderson (1974) discuss the adsorption of arsenic III and arsenic V onto both aluminum hydroxides and iron hydroxides. For both adsorbents, arsenic V species adsorption followed a Langmuir isotherm, and the adsorption of arsenic III species varied linearly with concentrations. Holm and others (1979) investigated the rates of removal of individual arsenic surface species and phosphate through adsorption and precipitation. The results of their study indicate the following:

PO_4	AsO_4	MMAA	AsO_3	DMAA
most strongly removed				least strongly removed

Adsorption data for all species, with the exception of arsenite, were found to follow Langmuir isotherms.

Biological transformations of arsenic species may be divided into two basic groups: methylation (Challenger, 1945) and production of volatile arsines (McBride and Wolfe, 1971). Challenger identified the formation of trimethyl arsine by fungi acting on inorganic arsenic. McBride and Wolfe have reported the ability of methanogenic bacteria to transform inorganic arsenic to methyl and dimethyl arsines. Ehrlich (1963), and Turner and Legge (1954), found that bacterial actions were related to the release and oxidation of arsenic from realgar and orpiment.

METHODS

FIELD PROCEDURES

Ground Water Sample Collection

Each water supply system was flushed for five minutes prior to collection of the untreated water samples. Samples were obtained directly from pump discharge, in some cases passing through a hydro-pneumatic tank. All samples for arsenic and ferrous iron analysis were preserved at the time of collection with HNO_3. A macro pipet was used to add 0.2 ml of "Ultrar" (Hopkins and Williams, Essex England) to each 100 ml of sample. Samples were collected and stored in Nalgene linear polyethylene containers having a polypropylene cap. Storage was at room temperature (25°C). A millipore filter apparatus with a 0.45 micron filter element was used for field filtration on selected samples. Vacuum was provided through the use of a "Mighty Vac" hand powered pump.

pH, Dissolved O_2, and Dissolved CO_2

The pH measurements were made at the time of sample collections. An Orion Research, Model 401 specific ion meter was used in conjunction with a Fisher Micro-Combination pH electrode. The instrument was calibrated with pH 4, 6, and 7 buffers prior to each reading.

Dissolved oxygen levels were determined directly in the pump discharge pipe. A Yellow Springs Instruments Model 51B, Oxygen Meter provided instrumentation. Calibration of this field meter was with air.

Dissolved carbon dioxide was measured with an Orion Research Model 95-02, carbon dioxide electrode, and Orion Research Model 401 specific ion meter.

Measurement of Static Water Levels

An electric sounder and standard steel tape were used to measure

water levels in accessible wells. Each measurement was made to the nearest 1/4 inch. The electric sounder consists of a weighted electrode having a 300 foot, two conductor drop line. The drop line is calibrated at five foot intervals. A hand held ameter is connected to the system and responds when the electrode is immersed in water. The steel tape is used to interpolate the five foot intervals.

Aquifer Pumping Tests

The Theis non-equilibrium method was used for aquifer evaluation. This method has been described by Todd (1959), and Freeze and Cherry (1979) and was utilized to determine the aquifer characteristics S (coefficient of storage) and T (transmissivity). This method is valid and useful under the following set of assumptions: the aquifer is homogeneous, isotopic and is of infinite areal extent; the well penetrates the entire aquifer; and the aquifer is confined. It is also assumed that the well diameter is infinitesimal and that the water removed from storage is discharged instantaneously with decline of head.

Values for S and T were determined from data obtained by pumping tests. In the first test, the intermediate school well was discharged at a constant 54.5 gallons per minute and the difference in water level from the static water level (h_o-h) at the elementary school well with time (t) was measured. The distance r between the two wells is 271 feet. The pumping test continued for 4.188 hours, at which time the system was nearly at equilibrium. In the second test, the intermediate school well was also pumped at 54.5 gpm. However, the observation well was located at the high school, a distance r of 1,125 feet. The data are listed in Table 3.

Values of r^2/t are plotted against the values of h_o-h and values for u are plotted against values for W(u), a well function (Figure 7). Both

Table 3. Pumping test data. Pumped well - Intermediate School.
Test 1: Observation Well - Elementary School, r = 271 feet.

Test 2: Observation Well - High School, r = 1125 feet,

Test 1		Test 2	
t (day)	h_o-h (feet)	t (day)	h_o-h (feet)
0	0	0	0
.0049	0.17	.0035	0
.0111	0.92	.0090	0
.0229	2.13	.0292	0.02
.0347	2.88	.0472	0.08
.0451	3.38	.0646	0.17
.0555	3.56	.0854	0.21
.0722	4.13	.1132	0.25
.0868	4.33	.1618	0.40
.0993	4.56	.1826	0.46
.1111	4.71		
.1236	4.88		
.1368	4.96		
.1507	5.04		
.1688	5.13		
.1861	5.21		
.2035	5.29		

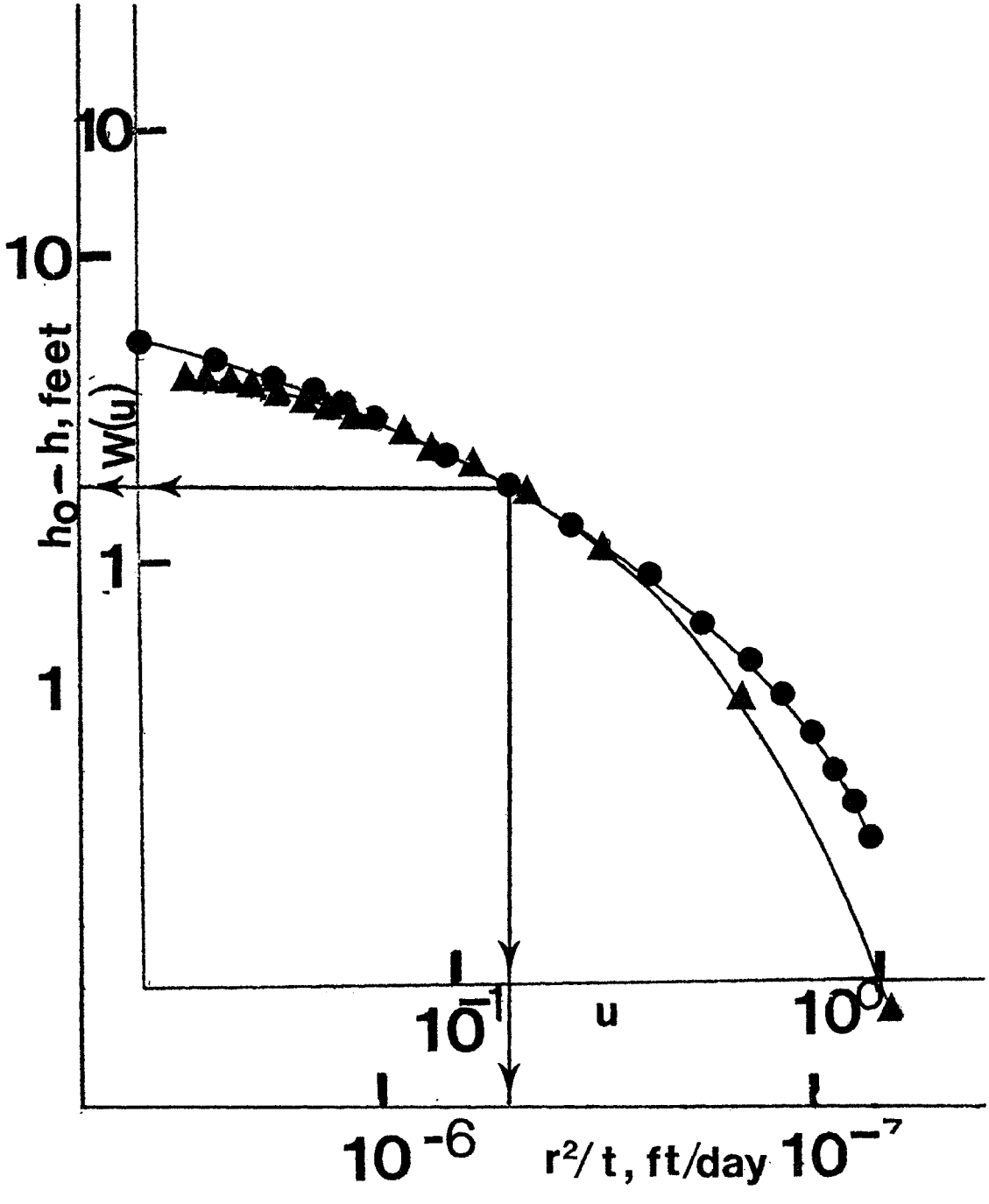

Figure 7. Two superimposed curves: r^2/t vs $h_o - h$; and u vs. W(u) for pumping test. Pumped well: Northwest Intermediate School. Observation well: Northwest High School.

u and W(u) were obtained from Todd (1959). Both sets of points are plotted on full log paper. Curves are superimposed with graph axis parallel, and a point is selected along a coincident segment. This match point is used for reference on each curve. Appropriate r^2/t, h_o-h, u, and W(u) coordinates are determined for the match points. T and S are determined from the following equations (Todd, 1959):

$$T = \frac{114.6\ Q}{h_o-h}\ (W(u))$$

and $$S = \frac{uT}{1.87\ r^2/t}$$

$T = 3{,}230.5$ gal/day/ft (first test)

$= 573.4$ gal/day/ft (second test)

$S = 1.2729 \times 10^{-4}$ (first test)

$= 1.5332 \times 10^{-5}$ (second test)

The results of the second pumping test were probably affected by a storm front that was moving through the vicinity at the time of the test. This test did, however, establish the premise of aquifer continuity between the wells of the elementary, intermediate, and high school.

ANALYTICAL METHODS

Total Arsenic

Total arsenic was determined by flameless atomic absorption spectrophotometry using a Perkin Elmer Model 603 spectrophotometer and a Perkin Elmer Model HGA-2100 heated graphite atomizer, equipped with a deuterium arc background corrector. The line source was an arsenic electrodeless discharge lamp at 193.7 mm. Instrument settings were as specified in the manufacturer's operation procedure. Temperature programming consisted of:

drying at 120°C for 60 seconds, charring at 1100°C for 20 seconds, and atomizing at 2400°C for 8 seconds. Peak area was read for 3 seconds during atomization. An interrupted argon purge at 20 cc/min. was used. Sample injection volume was 25 µl, preceeded by 5 ul of 1000 mg/l $Ni(NO_3)_2$ for matrix modification. Total dissolved arsenic data are listed in Table 4.

Inorganic Arsenic Speciation

Inorganic arsenic (III) was determined directly with differential pulse polarography. The method was adopted from Henry, Kirch, and Thorpe (1979). Instrumentation consisted of a Princeton Applied Research Corporation, Model 174A polarographic analyzer with an X-Y chart recorder. The sample was acidified with 1 M HCl at time of collection and stored at 0°C.

Polarographic conditions for the analyzer were:

working electrode: DME

reference electrode: SCE

counter electrode: Pt. wire

drop time: 2s

initial potential: -0.20 V

potential range: 0.75 V

scan rate: 1mV/s

modulation amplitude: 100 mV

Inorganic-Organic Arsenic Determination

Ion exchange chromatography and flameless atomic absorption spectroscopy were utilized to differentiate the following fractions: total inorganic arsenic (arsenate + arsenite); monomethyl arsonic acid; and dimethyl arsinic acid. The method was adopted from Iverson, Anderson, Holm, and Stanforth (1980), which was a modification of the method of Yamamoto (1975). Exchange

Table 4. Total arsenic concentrations. Station locations are listed numerically in the Appendix.

Station	As_{tot} (ppb)	Station	As_{tot} (ppb)	Station	As_{tot} (ppb)
1	<1	33	<1	69	3.
2	115.3	34	<1	70	3.
3	94.5	35	3.3	71	12.22
4	9.8	36	<1	72	28.05
5	33.0	37	<1	73	15.95
6	<1	38	<1	74	10.91
7	85.7	39	2.43	76	7.33
8	13.9	40	<1	77	8.27
9	<1	41	<1	78	8.47
10	9.6	42	<1	79	6.38
11	1.6	43	<1	80	8.23
12	13.5	44	<1	81	6.95
14	9.45	45	1.36	82	13.73
15	9.65	50	4.	83	4.15
16	4.7	51	3.	84	6.45
17	<1	52	4.	85	4.18
18	<1	53	2.	86	2.46
19	6.6	54	3.	87	3.29
20	3.75	55	5.	88	3.19
21	<1	56	6.	89	2.25
22	<1	57	4.	90	4.55
23	<1	58	9.	91	2.54
24	3.28	59	5.	92	2.11
25	8.8	60	5.	93	3.97
26	5.25	61	6.	94	2.94
26A	9.01	62	4.		
27	13.77	63	7.		
28	2.05	64	8.		
29	4.31	65	8.		
30	<1	66	10.		
31	1.2	67	8.		
32	<1	68	2.		

columns were assembled in the laboratory. Standard 100 ml burets were carefully packed with 25 cm^2 of Dowex AG-50W-X8 (200 mesh) cation exchange resin (J.T. Baker Co.). Glass wool plugs were used to retain the resin beads at each end. Due to noted differences in exchange characteristics between columns, only one column was used for the final analysis. Columns were washed and reconditioned prior to each use with 25 ml of 1M NH_4OH followed by 50 ml of 1 MHCl. Dilute HCl (4%) was used to acidify the columns to pH 1.5. Resin used in columns was exposed to 50 ug of each As species prior to conditioning. Total arsenic values were known for the samples. Sample size was adjusted to 1 ug of total arsenic, the optimum amount for this method (Iverson, Anderson, Holm, and Stanforth, 1980). Sample pH was adjusted to 1.5. Samples were added to the columns and sequentially eluted with 30 ml of 0.2 M trichloroacetic acid and with 60 ml of 1 M ammonium acetate (NH_4CH_3COO). Fractions were collected at 9 ml intervals in polypropylene vials. Separate standards for arsenate, monomethyl arsonic acid, and dimethyl arsenic acid and an acidified distilled water blank were used for this analysis. Each fraction was analyzed for total arsenic using the atomic absorption spectroscopy method. Chromatograms were prepared from AA data for each standard (Figures 8, 9, and 10), and for the sample (Figure 11).

Chloride

Chloride concentration was determined by microtitration with mercuric nitrate. The method was modified from Standard Methods (1975). The colorimetric indicator-acidifier consisted of the following reagents dissolved in 100 ml of 95% ethyl alcohol:

a) 250 mg s-diphenylcarbozone

b) 4.0 ml concentrated HNO_3

c) 30 mg xylene cyanol FF

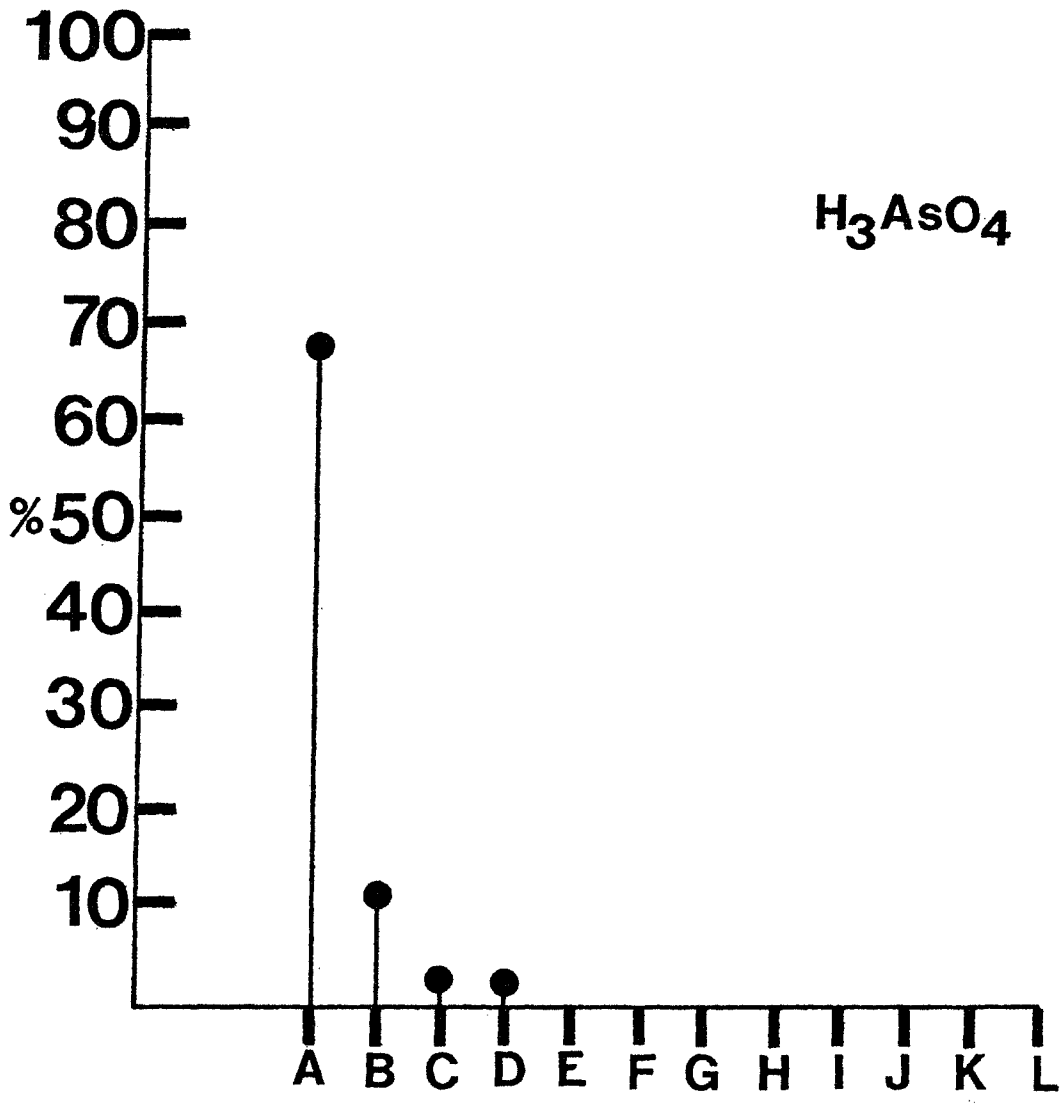

Figure 8. Chromatogram at 25°C and one atmosphere for arsenic acid.

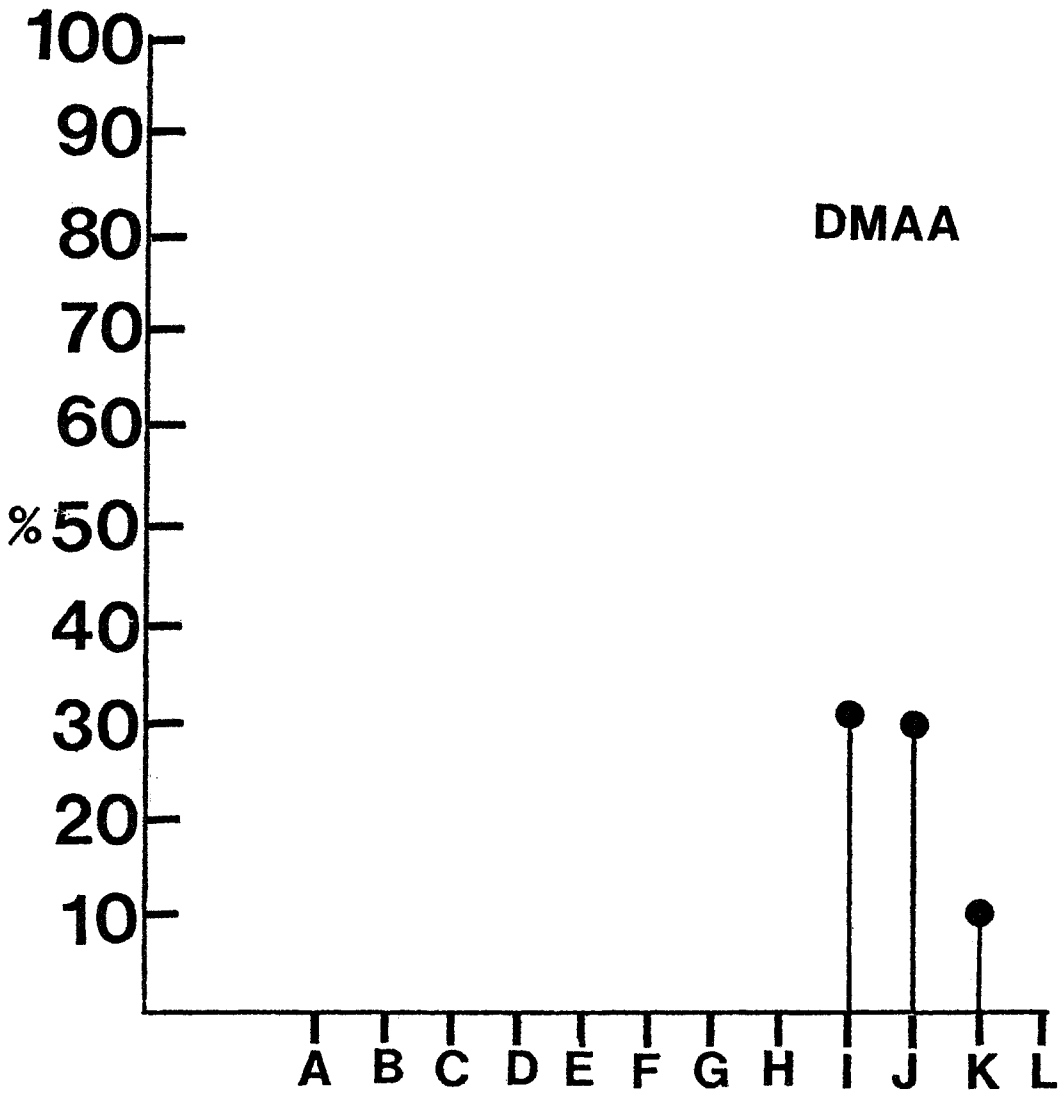

Figure 9. Chromatogram at 25°C and one atmosphere for dimethyl arsenic acid.

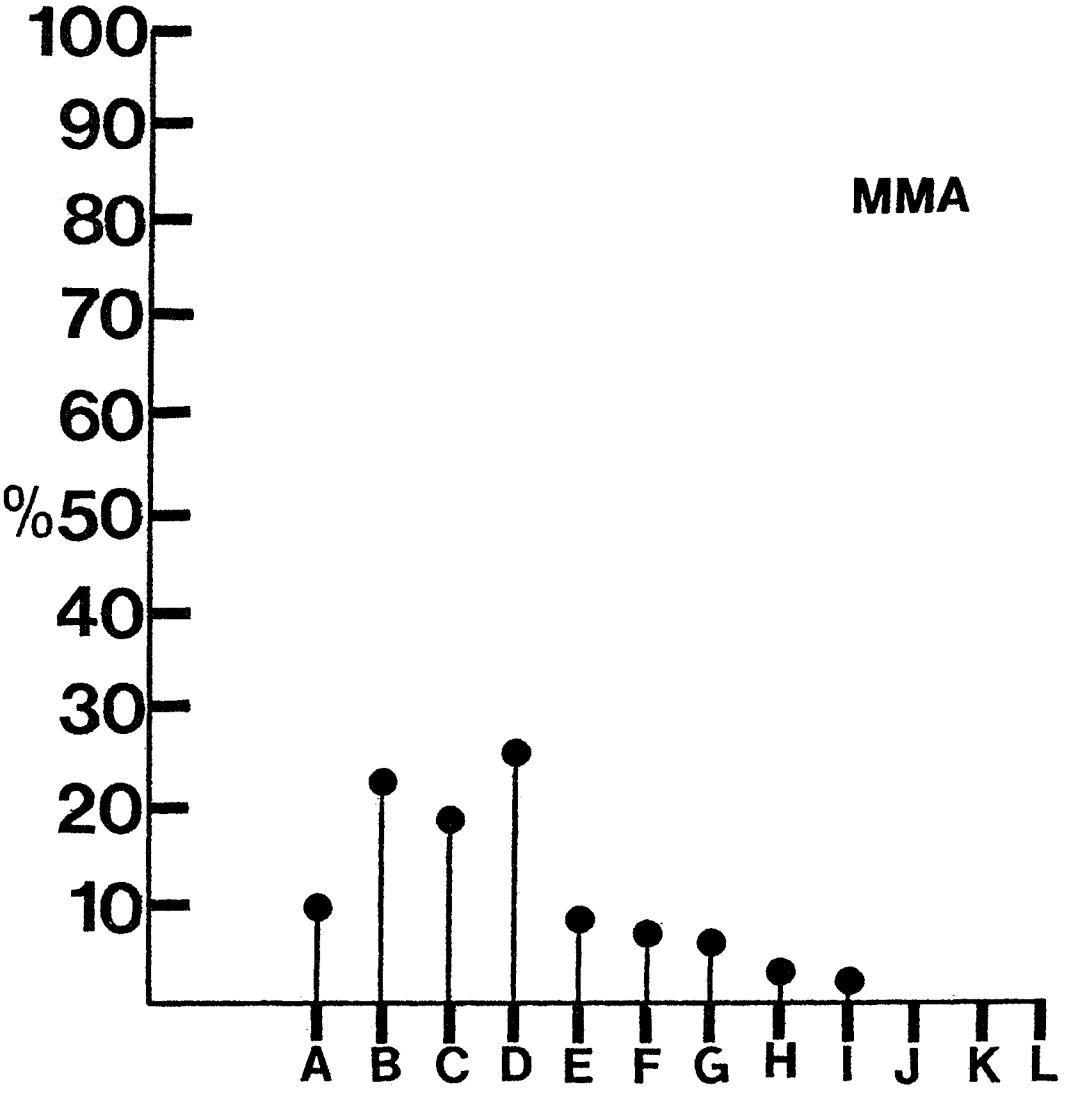

Figure 10. Chromatogram at 25°C and one atmosphere for monomethyl arsonic acid.

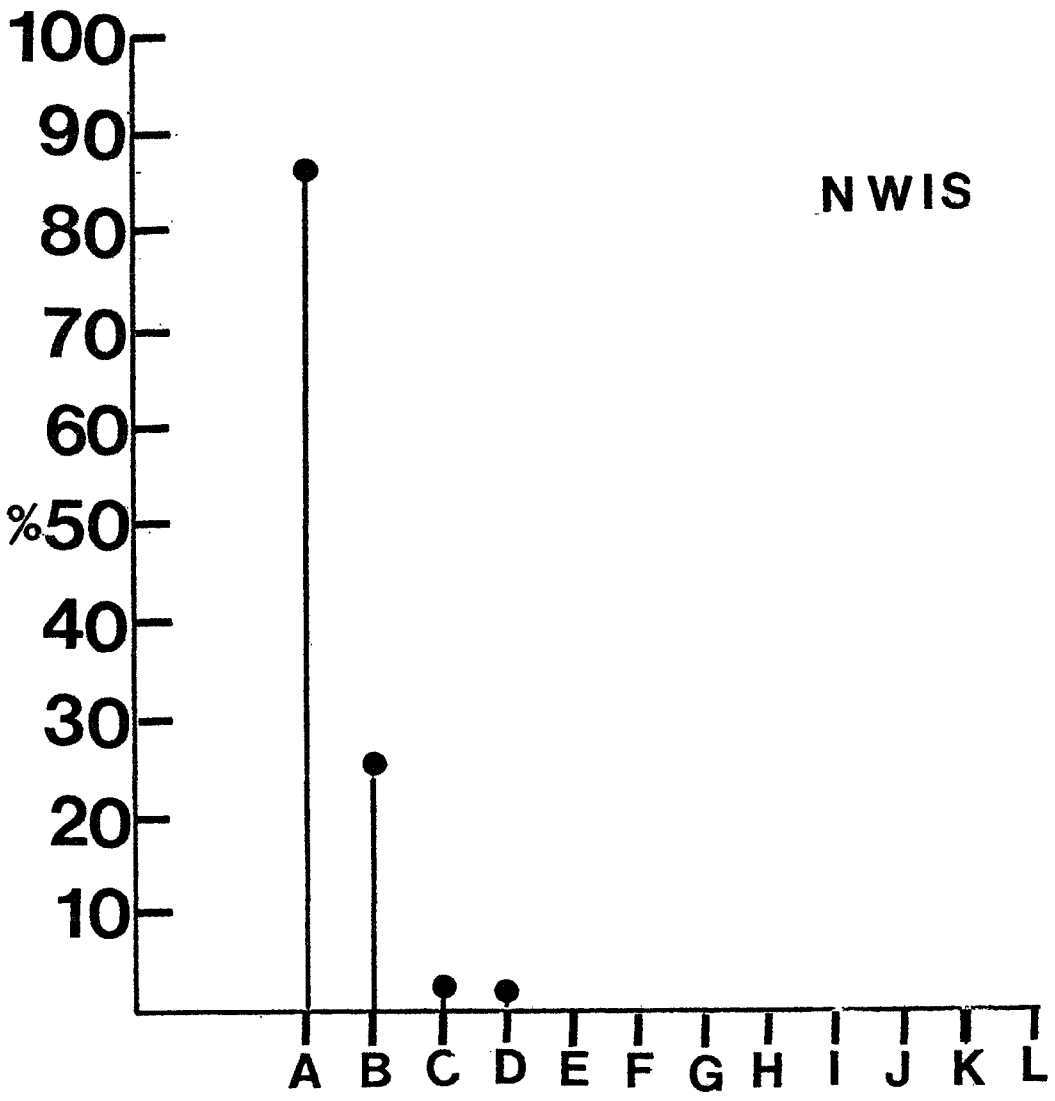

Figure 11. Chromatogram at 25°C and one atmosphere for a water sample collected from the well at the Northwest Intermediate School.

The mercuric nitrate titrant was prepared from 2.3 gm Hg $(NO_3)_2$ dissolved in 100 ml H_2O containing 0.25 ml concentrated HNO_3, and then diluted to 1 liter. Chloride standards of 1 ppm, 10 ppm, and 40 ppm were prepared from 1000 mg/l reference standard. To each sample and standard of 1 ml is added 10 ul indicator-acidifier. Chloride data are given in Table 5.

Ferrous Iron

Ferrous iron concentrations were determined by the phenanthroline method described by Troup (1974). Two ml of O-phenanthroline plus a sodium acetate/acetic acid buffer is added to 3 ml of sample immediately upon collection. An Fe(II)-phenanthroline colored complex is fully formed within 10 minutes and stable for at least 24 hours. Maximum absorption was read at 510 mm on the Beckman DU spectrophotometer within 12 hours of sample collection. Response is linear up to 4 ppm Fe(II); samples of greater concentration are diluted prior to analysis. Ferrous iron data are presented in Table 6.

Rock and Soil Samples

Samples of rock and soil materials were collected for a determination of their arsenic content. The sample preparation and bomb digestion of solids procedures are from Agemian and Chau (1975). Samples were ground to a fine powder passing a 270 mesh sieve. 100 mg of prepared sample was transferred to a teflon cup. Reagents were added in the following order: 4.0 ml nitric acid (70%); 1.0 ml perchloric acid (60%); and 6.0 ml hydrofluoric acid (48%). The bombs were sealed and heated for 3.5 h at 140°C.

At completion, the bombs were allowed to cool, and then the contents transferred to a 125 ml linear polypropylene bottle. Each bottle contained a solution of 4.8 g of boric acid in 30 ml H_2O to dissolve precipitated

Table 5. Chloride concentrations. Station locations are listed numerically in the Appendix.

Station	Chloride (ppm)	Station	Chloride (ppm)	Station	Chloride (ppm)
1		32	31.2	67	3.5
2	1.6	33	53.9	68	11.1
4	1.0	34	48.9	69	3.5
5	1.0	35	18.6	70	11.7
6	36.9	36	91.7	71	13.6
7	5.1	37	63.4	72	31.2
8	1.0	38	79.1	73	30.6
9	43.8	39	47.6	74	5.4
10	2.9	40	12.3	76	7.3
12	5.4	41	15.5	77	3.5
14		42	14.9	78	30.6
15	9.8	45	65.9	79	17.4
16	14.2	50	16.1	80	16.7
17	1011.	51	30.0	81	7.3
18	110.	52	36.3	82	6.7
19	53.9	53	13.0	83	9.8
20	16.1	54	14.2	84	18.6
21	36.3	55	9.8	85	91.7
22	22.4	56	14.9	86	6.0
23	13.6	57	134.5	87	9.8
24	6.0	58	13.6	88	21.2
25	5.4	59	16.1	89	26.2
26	4.8	60	32.5	90	45.7
26A	22.6	61	25.6	91	7.9
27	4.8	62	7.3	92	19.9
28	14.9	63	5.4	93	344.9
29	14.9	65	8.6	94	91.7
30	110.6	66	6.0		

Table 6. Ferrous iron concentrations. Station locations are listed numerically in the Appendix.

Station	Fe(II) (ppm)
2	7.77
4	0.896
5	2.20
12	0.869
16	0.101
17	0.106
25	1.20
27	0.264
60	1.32
67	0.711
71	0.618
72	0.411
73	0.264

metal fluorides. Each solution was transferred to a 100 ml volumetric flask and brought to volume with H_2O. Contents were transferred to 125 ml linear polypropylene bottles for storage. Total arsenic was determined by flameless atomic absorption analysis. The solid samples and their arsenic contents are listed in Table 7.

Table 7. Total arsenic concentrations in selected solid samples.

Solid Sample	[As] ppm
Weathered iron stained Sharon Sandstone - Chippewa Twp.	31.2
Sharon Sandstone - hematite bands removed - Chapin Forest	33.7
Hematite band from Sharon Sandstone - Chapin Forest	13.4
Weathered Sharon Sandstone - Chippewa Township	13.1
Marcasitic Sharon Sandstone - Chapin Forest	42.6
Sharon Sandstone - Barberton	0
Iron stained Sharon Sandstone - Chapin Forest	8.5
Suspended solids from Northwest Intermediate School water well discharge	334.8

GEOLOGY AND HYDROGEOLOGY OF THE STUDY AREA

GEOLOGIC SETTING

The geologic setting of the study area includes remnants of both Paleozoic sedimentation and Pleistocene glaciation. The Sharon Sandstone (Conglomerate) is the basal sedimentary formation of the Pottsville Series of the Pennsylvanian System in northeast Ohio. This formation was locally deposited within topographic lows of the erosional surface of the Wooster Shale Formation of the Cuyahoga Group, Mississippian System (Multer, 1955; Meckel, 1967). Due to the great relief of the Mississippian erosional surface (maximum 264 feet; Multer, 1955) younger members of the Pottsville Formation were deposited directly upon this surface at higher elevations where the Sharon was lacking.

A structure contour map prepared by Multer (1955) indicates a topographic low at the Mississippian-Pennsylvanian disconformable surface along the present valley of Chippewa Creek in northeastern Wayne County. This depression is oriented to present drainage and may be expected to continue into northwestern Stark County.

The Harrison Ore, a thin iron ore of variable lithology, has been discussed by several workers (Morningstar, 1922; Stout, 1944; Hall, 1951). This unit lies at the Mississippian-Pennsylvanian boundary, and, due to its unusual nature, merits some discussion. The mineralogy of the Harrison Ore is a product of solution diagenesis, and consists of limonite, siderite and/or marcasite in northeast Ohio (Fuller, 1965) and was described in southern Ohio by Hall (1951) as a ferruginous conglomeritic sandstone. The Harrison, wherever observed, is stratigraphically positioned at the Mississippian-Pennsylvanian disconformity (Hall, 1951; Fuller, 1965). The origin of the clastic matrix of this unit has not been fully resolved.

Morningstar (1922) suggests that it is reworked Mississippian sediment with deposition Pennsylvanian in age. Stout (1944) assigns the Harrison Ore to the post-Mississippian, pre-Pennsylvanian erosion interval. Hall (1951) placesthe Harrison ore in southern Ohio at the base of th Pennsylvanian but notes that this member does not have a definite time-stratigraphic position as it may be directly overlain by various-aged members of the Pottsville Formation. Multer (1955) describes the Harrison Ore in Wayne County as being a sandy, argillaceous (iron-banded, fine-grained silty sandstone) nodular ore of two or three inches in thickness. In southwestern Wayne County the Harrison Ore is represented by fragments of iron ore and iron-stained cherty limestone.

The Sharon Sandstone is generally a pure, medium-grained orthoquartzite throughout its area of outcrop in northeast Ohio (Fuller, 1955). The silica content of this sandstone is reported to average 96 to 97% (Fuller, 1955; Mrakovich, 1969). The thickness of this sandstone in northeast Ohio varies from 0 to 170 feet, and deposition was largely controlled by the topography of the Mississippian erosional surface (Fuller, 1955). Pebbles composed of limestone and fossiliferous limestone containing corals of the Middle Devonian Period have been described from this member (Fuller, 1955; Meckel, 1967). The two principal impurities in the Sharon Sandstone are aluminum oxide and iron oxide (Fuller, 1947). Within the Sharon of northeast Ohio, four isolated conglomeritic belts have been described (Lamb, 1941; Fuller, 1955). These belts are oriented in an approximate north to south direction, are 1000 feet or less in width, 10 to 50 feet in thickness, and have been mapped to a maximum of seven miles in length (Fuller, 1955). Cross stratification within the Sharon Sandstone (orthoquartzite) and its conglomerate phase are described by Fuller (1955) and Mrakovich (1969) as

planar, with cross beds dipping southward. At some localities planar cross bedding has been altered by erosion to trough cross bedding. Bed thickness varies from 2 inches to 15 feet (Fuller, 1955). By considering the areal distribution, bedding features, mechanical analysis, fossils, mineralogy and regional structure, Fuller (1955) and Meckel (1967) indicate a northern source area for the Sharon Sandstone of northeast Ohio. A Canadian highland of metamorphic and some Devonian age sedimentary rocks is suggested by Fuller (1965).

The Sharon Sandstone is overlain by the Sharon Shale (Pottsville) and the Sharon Coal (Multer, 1955). The coal has been mined within the field area through underground mining in the late 19th and early 20th centuries.

PLEISTOCENE GEOLOGY

The topographic and sedimentary features of the study area were greatly influenced during the Pleistocene. Drainage reversals, topographic alteration of the bedrock surface, and the deposition of a complex sequence of tills, outwash, and alluvium all occurred during this epoch.

The history and development of drainage is discussed in detail by VerSteeg (1934) and Winslow *et al.* (1953). The Teays drainage system of the Late Tertiary developed at the time of the Parker strath. This system flowed predominantly from south to north. Ice damming of Teays drainage during early Quaternary time resulted in formation of lakes and the eventual reversal of drainage. The Tuscarawas and the Cuyahoga Rivers of northern Ohio were channels of the Teays system and may have been contiguous. Deep Stage drainage developed due to the obstruction and reversal of the Teays system. Stream flow was now oriented westward and some channels, including the Ohio River, downcut 200 feet below their level of the Teays stage.

The beginning of the Illinoian glaciation is considered to be the termination of Deep Stage drainage. Pre-Illinoian valleys were filled by outwash and till, with outwash deposits extending beyond the limits of till deposition. Wisconsin drift continued the filling and covering of the pre-Illinoian valleys.

Present drainage is essentially unchanged from that at the close of the Wisconsin glaciation. The Tuscarawas River flows south within the Ohio River Basin and the Cuyahoga River flows north to the Lake Erie Basin.

White (1960) refers to the glacial tills of northeast Ohio as rock-stratigraphic units, and assigns the tills of the study to the Killbuck glacial lobe (White, 1961). The stratigraphic sequence from oldest till to youngest till is: the Millbrook till, the Navarre till, and the Hayesville till. The Millbrook till (Illinoian or Wisconsin stage, unresolved) is directly underlain by Mississippian and Pennsylvanian rocks. This till is sandy, pebbly, and has a characteristic brown color. The Navarre till of the Wisconsin stage directly overlies the Millbrook till or is found directly upon bedrock. Navarre till is sandy and pebbly, with some cobbles and boulders, and has an oxidized color of yellow brown. The Hayesville till, Wisconsin stage, has been mapped by White (1961) as the surficial material within the study area. Hayesville till is silty with a variable pebble content and contains few cobbles and boulders. The oxidized color of Hayesville till is dark brown.

Water well logs were used to construct the sursurface geology at the study area. Figure 12 illustrates the locations of buried valleys, and Figure 13 shows the relationship (in cross section) of the buried valley deposits and the consolidated rock-stratigraphic units.

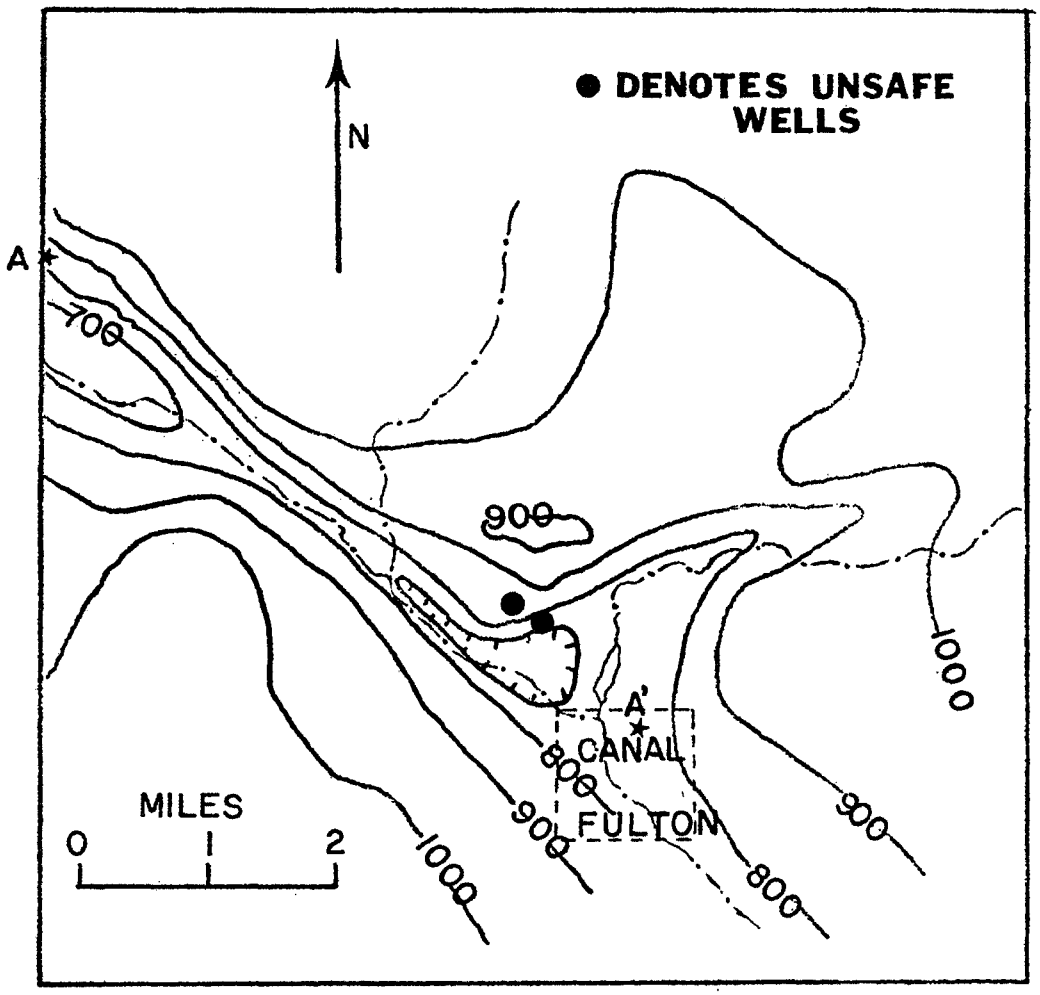

Figure 12. Location of buried valleys within study area. Cross section transect indicated by line A-A'

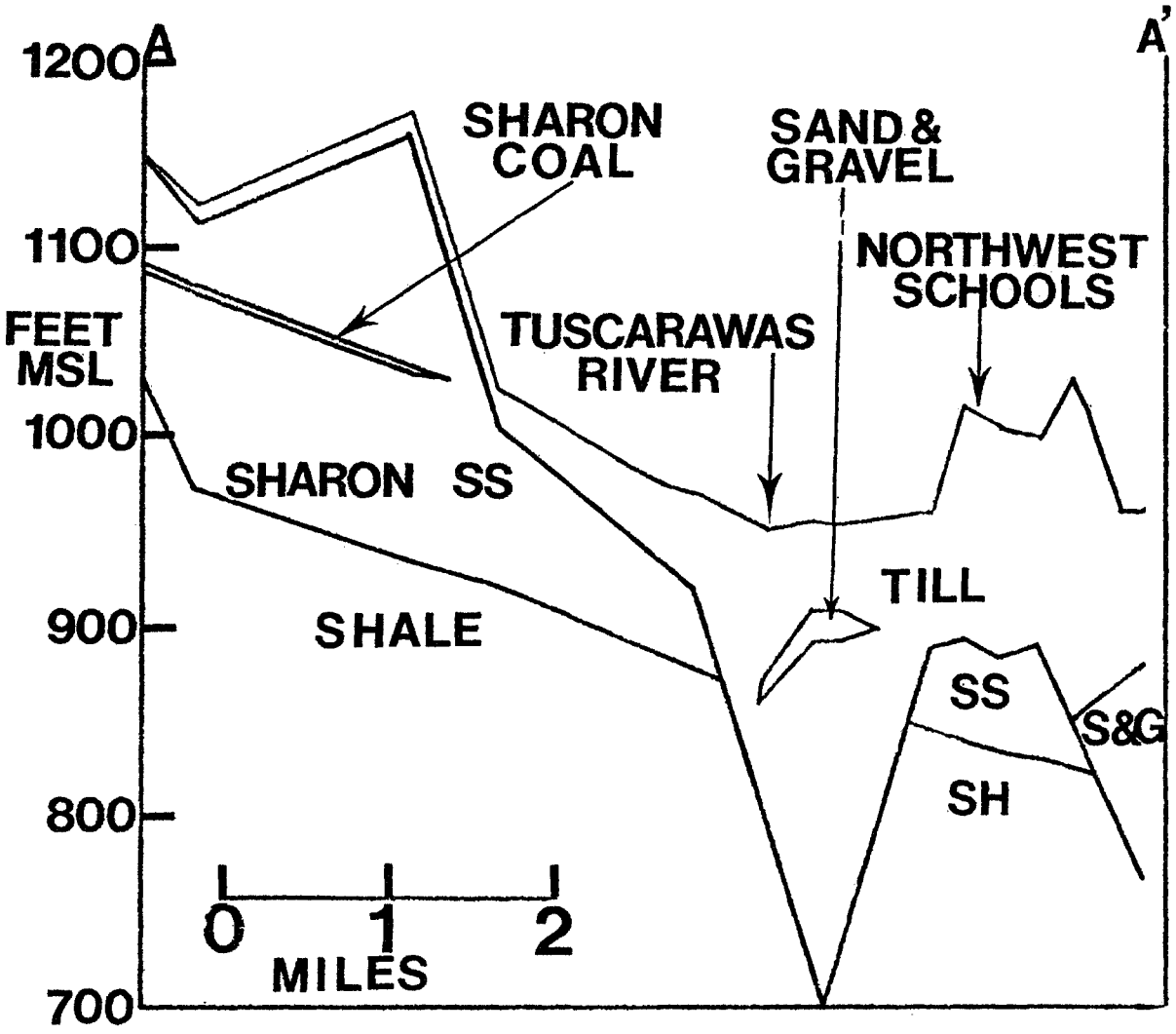

Figure 13. Cross section A-A', as located in Figure 12, indicating relationship of consolidated and unconsolidated rock stratigraphic units.

HYDROGEOLOGY OF THE STUDY AREA

Two major aquifer systems exist within the study area: The Sharon Sandstone of the upland areas; and the outwash sand and gravel deposits of the buried valleys together provide adequate ground water supplies for municipal, institutional, farm, and domestic use. Shales of the Cuyahoga group underlie the entire study area and are considered to be a third aquifer system. Wells developed within the Cuyahoga group are generally of small yield.

The precise thickness of the sand and gravel deposits has not been logged, as most wells developed in this artesian aquifer obtain adequate yields within the top ten feet of outwash. Available data indicates a potential total thickness of the outwash deposit of about 200 feet. Artesian conditions exist within this aquifer due to the effects of a confining stratigraphic unit and the local hydraulic gradient. The confining unit is a clay till that ranges in thickness from 20 to 217 feet and has a mean thickness of 83 feet (from 29 well logs). Till is generally overlain by recent alluvial deposits.

The configuration of the buried valley outwash aquifer is illustrated in Figure 12. The principal buried valley extending from the southeast to the northwest has developed within the course of the Teay stage "Dover River" (VerSteeg, 1934 and White, 1953). The Tuscarawas River and the Chippewa Creek now flow along the surface of this valley fill. The bedrock surface of the Dover River is near the 700 foot (MSL) elevation, and slopes northwest.

The present course of the Tuscarawas River north of Clinton, and the present course of Nimisila Creek are both underlain by buried valleys of a lesser magnitude. Both developed within unnamed Teays stage tributaries

of the Dover River. Municipal wells developed within this buried valley aquifer are located at Canal Fulton, Stark Co., Rittman, Wayne Co., and Lodi, Medina County.

The consolidated rock aquifer system of the Sharon Sandstone has a mean thickness of 74 feet. The Sharon Sandstone is the sole source of ground water for the wells of the school complex. This unit is underlain by shales of the Cuyahoga Group, of the Mississippian System which represent a separate aquifer system capable of providing limited yields for farm or domestic use (White, 1953).

A confining stratigraphic unit of clay till overlies most of the surface of the sandstone aquifer. This unit ranges in thickness from 0 to 190 feet. The till is absent or very thin west of the Tuscarawas River and north of the Chippewa Creek, and is thin east of the Tuscarawas River in southern Franklin Township. Both areas are of maximum elevation within the study area. The mean thickness of the till over bedrock is 49 feet.

Artesian conditions are generally present within the bedrock aquifer system throughout the study area, except north of the Chippewa Creek to the west of Clinton.

The sandstone aquifer system is divided by the buried valley aquifer system as is illustrated by Figures 12 and 13. Boundary conditions have developed at the margin of the buried valley system. Both recharge and barrier boundary conditions exist within this array of aquifers and aquitards. A recharge boundary to the Sharon Sandstone is indicated to the southeast of the school complex. Saturated sand and gravel outwash within the buried valley of Nimisila Creek have been shown through analysis of well logs to be adjacent to the Sharon Sandstone. The existence of a

barrier boundary to the Sharon Sandstone is also indicated by well log analysis. This boundary is located west of the school complex at the margin of the buried valley of the Tuscarawas River. A stratigraphic unit of clay till has been deposited adjacent to the Sharon Sandstone. This boundary may vary, as saturated sand is indicated to be opposite the Sharon southwest of the school complex. The combined potentiometric surface of the consolidated rock aquifer system and the Minisila Creek buried valley aquifer is illustrated by Figure 14. The assumption is made that these aquifers are interconnected at a recharge boundary, and therefore one figure is utilized to represent the potentiometric surface at both aquifers. From Figure 14, the direction of ground water flow is indicated to be northeast to southwest, having an average gradient of 29 feet per mile (0.0055 ft/ft).

Chloride concentrations were determined for 82 water wells within the study area to trace the sources of the ground water. The current and historical chloride contamination of the Tuscarawas River will have tagged any ground water recharge from this source with high levels of chloride. Concentrations ranged from less than one ppm to 1011 ppm, having a mean value of 41.8 ppm (Table 5).

Results (Figure 15) indicate that minimum values for chloride concentration accompany the most severely arsenic contaminated wells. When all wells are considered, however, no true inverse relationship is found comparing chloride versus total arsenic. Recharge to the local aquifer system from the Tuscarawas River may be occurring in the north-central portion of the study area. A chloride plume is clearly developing in this area. It is clear, however, that the current source of recharge for the high arsenic wells is not the chloride contaminated Tuscarawas River.

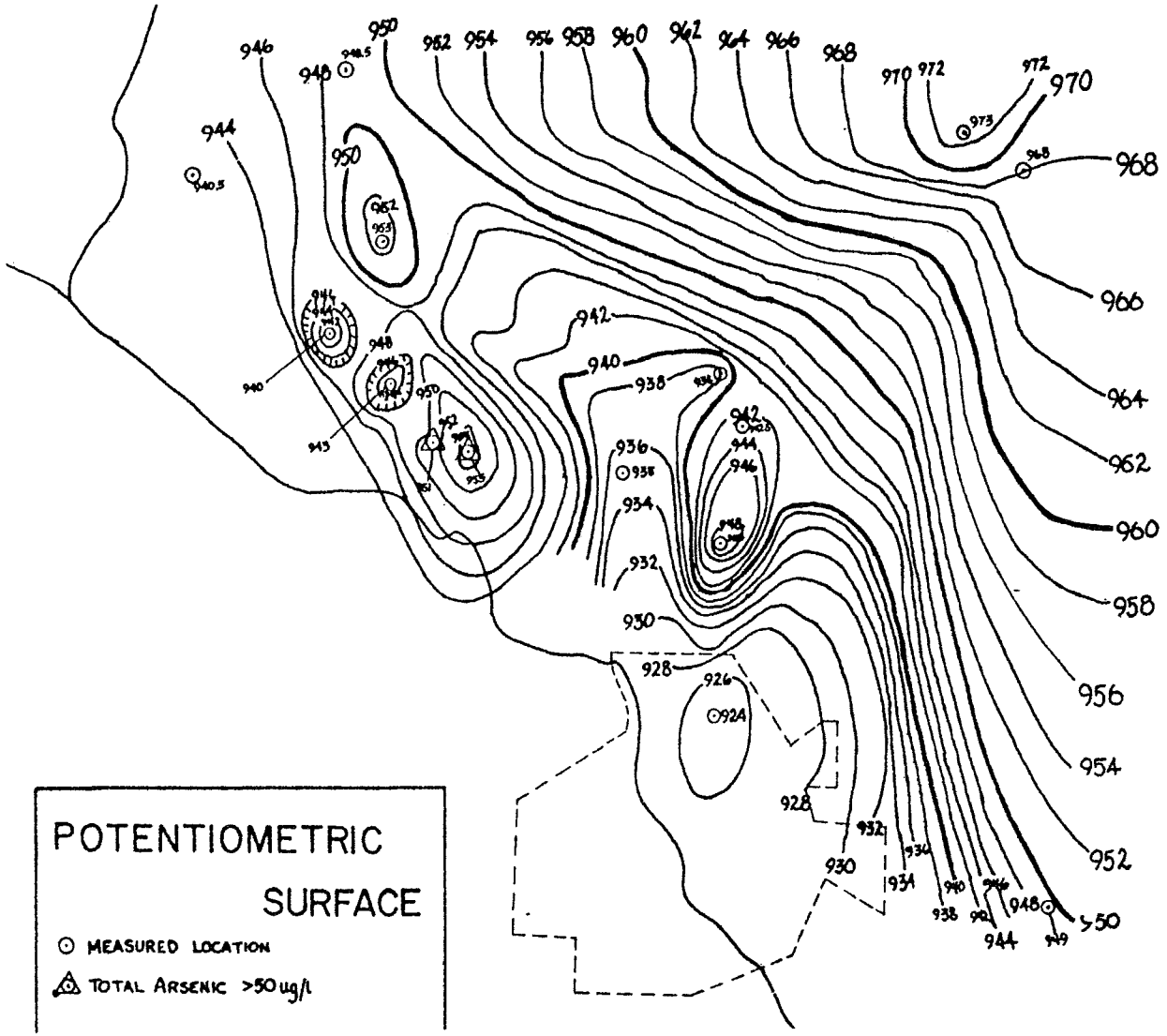

Figure 14. Combined potentiometric surface of consolidated rock aquifer system and Nimisila Creek buried valley aquifer system.

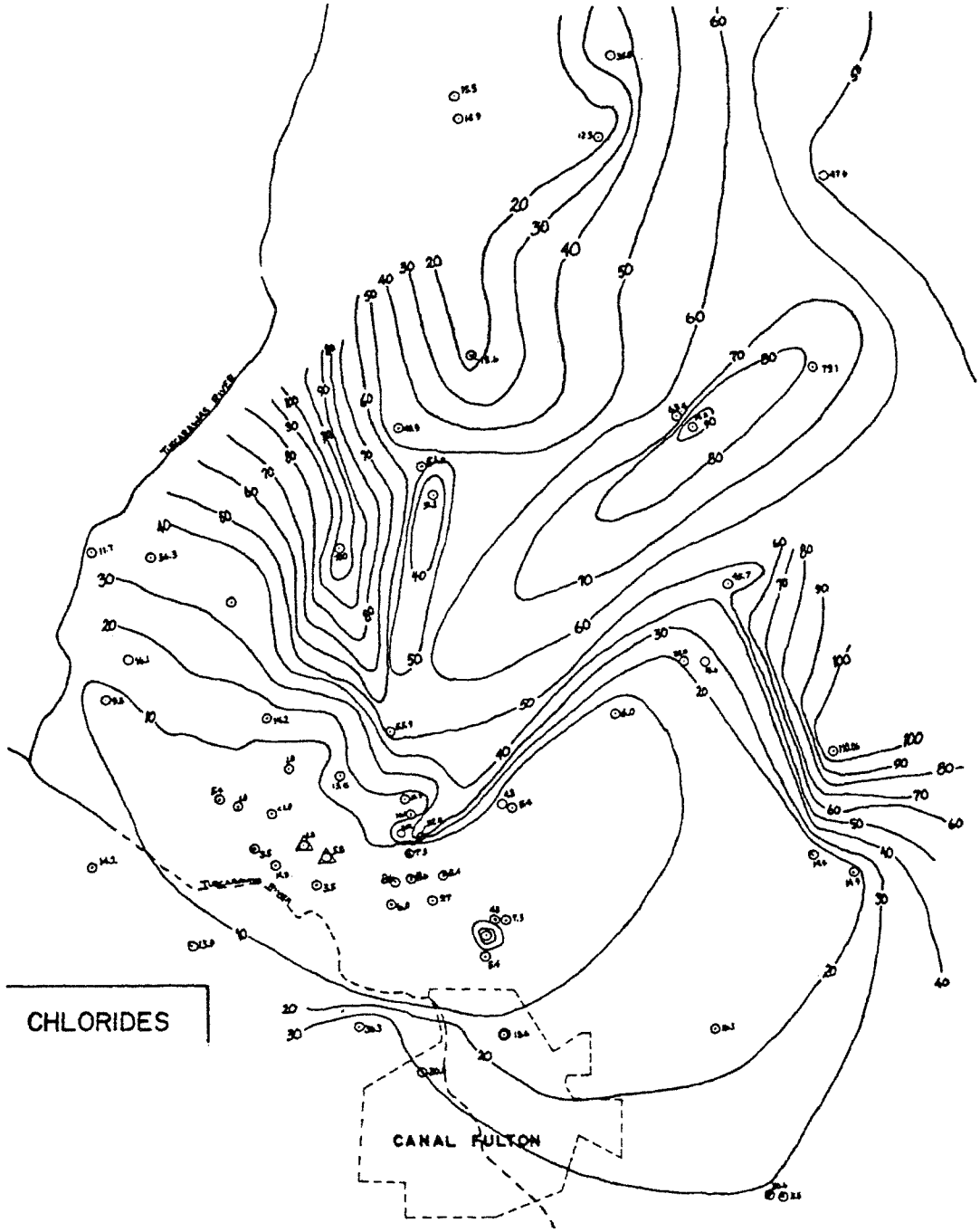

Figure 15. Areal distribution of chloride within the study area.

Total arsenic concentrations were determined for 88 wells within the study area. The concentrations ranged from 0-96 ug l^{-1} (Table 4).

The areal distribution of arsenic within the study area is illustrated in Figure 16. The zone of elevated arsenic levels (above background of less than 1 mg l^{-1}) is clearly a defined and restricted area. Maximum and unsafe arsenic levels within this zone are shown as peaks at the Northwest Intermediate School and Elementary School wells. Peaks are also evident at the well field of the village of Canal Fulton. These latter arsenic levels are considered safe as they are below the maximum contaminant level of 50 ug l^{-1}. The iso-concentration map for arsenic gives no indication of an outside source of arsenic for the study area. No plumes of arsenic contamination are entering the study area from outside sources.

Within the study area, there are no confirmed anthropogenic sources of arsenic. Under Ohio EPA and U.S. EPA investigations, however, (initiated as a result of this study), is an abandoned industrial dump site referred to as the "Comet Road Dump Site". Surface water analysis at this site indicated the presence of arsenic. As this site is situated above the buried valley aquifer of Nimisila Creek, test borings are currently proposed to establish the precise nature of the underlying unconsolidated materials (glacial drift and alluvium) in order to assess potential interactions with the underlying sand and gravel aquifer. Ground water samples will be collected from test holes.

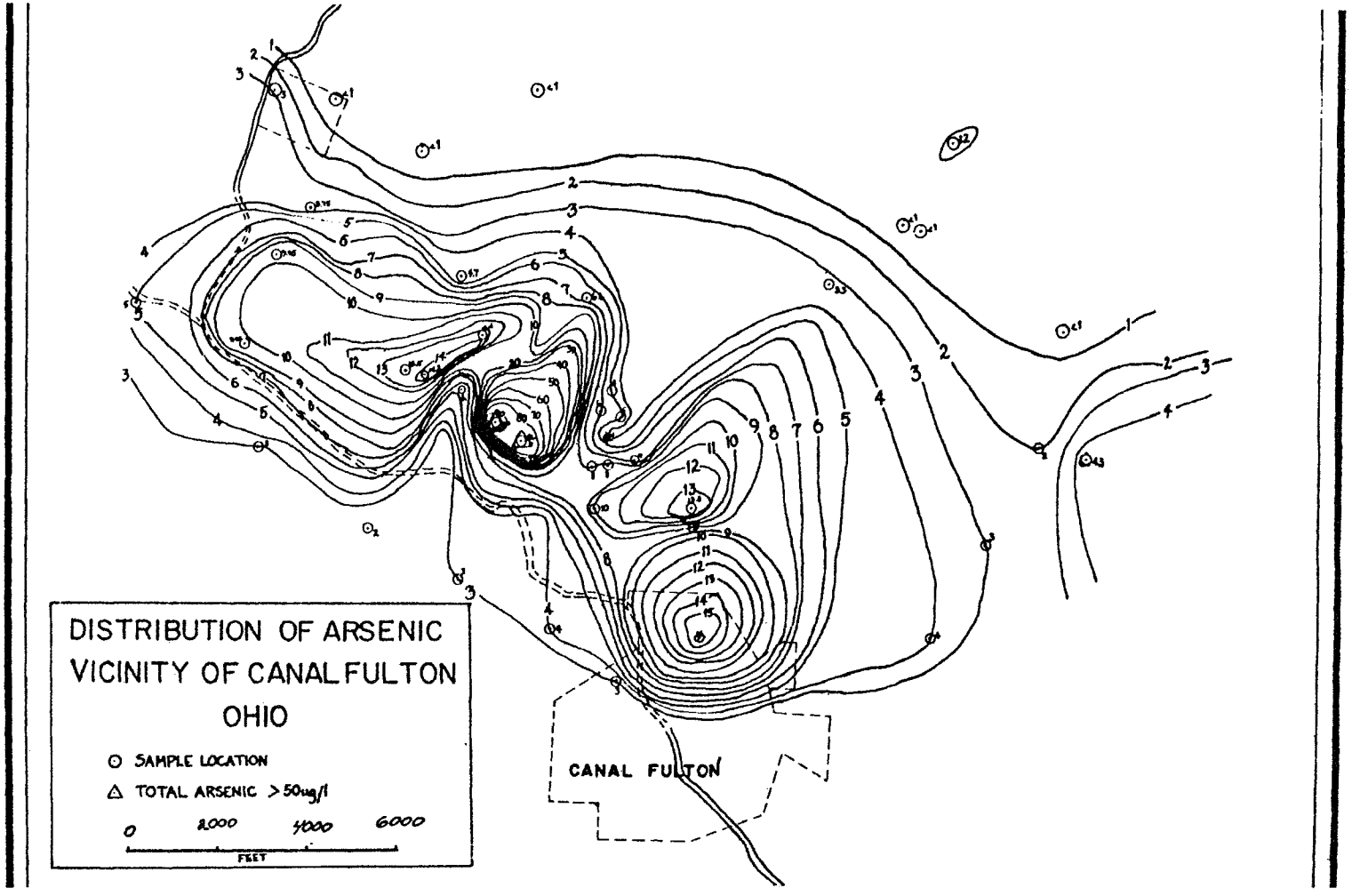

Figure 16. Areal distribution of arsenic within the study area.

DISCUSSION

Arsenic in Ohio ground water has not been previously reported. Thus at the onset of this investigation, sources of anthropogenic arsenic from agricultural, mining, and industrial activities were all considered. Agricultural soils were analyzed and found to contain no elevated levels of arsenical residues. The industrially contaminated Tuscarawas River and the large industrial impoundments to the north were eliminated as a result of the chloride and arsenic surveys. Mine drainage from abandoned underground coal mines west of Clinton contained no significant levels of arsenic. One potential anthropogenic source, the "Comet Road Dump Site", is under a continuing investigation, but at this time there is not sufficient evidence to implicate this site as the source of arsenic contamination at the school wells. The arsenic contamination is too widespread to implicate a point source caused by a prank or vandalism at the schools.

The potential exists for natural aquifer materials to provide a source of arsenic. Arsenic may be accumulated within the Sharon Sandstone by adsorption onto hydrous iron oxide cement at sand grain surfaces, or by incorporation into iron sulfide minerals through isomorphous substitution. The hydroxides are present as impurities (Fuller, 1947) and along with some clay minerals, adhere to the surface of the silica grains and act as a cement. Elution studies of Gulens, Champ and Jackson (1979) demonstrate the immobilization of arsenic through adsorption to hydrous oxide surfaces. Adsorption is controlled by Eh-pH conditions, and the adsorption of arsenic V and arsenic III may vary with respect to each other as these conditions are varied.

The stability of iron hydroxides must also be considered as a possible controlling factor in arsenic adsorption and desorption. At the

given conditions of pH = 7 and Eh = 0.016 volts, and where total iron equals 4×10^{-4} moles liter^{-1}, iron (III) hydroxide and Fe(II) are near an equilibrium condition. Thus, minor changes in Eh or pH can significantly impact the stability of the solid hydroxide phase. As Eh or pH is increased, $Fe(OH)_3$ is favored, and as Eh or pH is decreased, Fe^{+2} is favored, i.e. dissolution of the solid phase. Any adsorbed arsenic will be released to the solution upon dissolution of the iron hydroxide. Analysis of suspended solids from the water supply well of the Northwest Intermediate School indicate that arsenic concentrations within this fraction are high (334.8 mg l^{-1}). The source of these solids is most likely the ferric hydroxide cements of the Sharon Sandstone.

The apparent adsorption of arsenic species by ferric hydroxide may involve both adsorption and the formation of iron-arsenic complexes. Such complexes were experimentally studied by Gulens, Champ and Jackson (1979). The results of their work indicate that the iron (III)-arsenic (III) and (V) complexes are precipitated in solution, and the solubility of these complexes varies with pH and arsenic oxidation state. The solubility of the arsenic (V)-iron (III) complex decreases as pH is lowered, and the solubility of the arsenic (III)-iron (III) complex decreases as pH is increased. Wagemann(1978) approaches the formation of metal arsenic complexes through thermodynamics, and concludes that ferric arsenate will control total dissolved arsenic only at low pH conditions (pH < 2). Ferric arsenite (Fe III - As III) was not considered. Ferguson and Gavis (1972) consider the thermodynamic stability of ferric arsenate and limit its region of stability to pH less than 2.3, and Eh greater than +0.74 volts. Each worker concurs on the low pH insolubility of ferric arsenate. However, the higher pH insolubility of ferric arsenite is noted only by

Gulens, Champ and Jackson (1979), and has not been discussed using thermodynamics. However, their experimental results indicate a high solubility of the arsenic III-iron III complex. A value for the Gibbs free energy of $FeAsO_3$ is currently lacking in the literature, thus precluding a thermodynamic approach for this complex.

The exceptionally high concentration of ferrous iron in the arsenic contaminated waters of the Northwest Intermediate School may indicate the solution of an iron oxide solid phase. Existing ground water conditions indicate that this hydrogeochemical system is very near an Eh-pH boundary with respect to Fe^{+2} and $Fe(OH)_3$. Relatively minor changes in Eh or pH can significantly alter the stability and predominance of either species. An expanded scale Eh diagram at pH = 7 was prepared for arsenate/arsenite ratios ranging from 100 to 0.01 (Figure 6). The stability boundary that exists between ferric hydroxide and Fe^{+2} ion is indicated for ferrous ion concentrations of 10^{-4}, 10^{-5}, and 10^{-6} moles $liter^{-1}$. This diagram illustrates in detail the "redox window" of Cherry and others (1979) for the given arsenic couple. The entire set of values on this diagram is within a range of 0.122 volts.

The model of dissolution for ferric hydroxide resulting from a minor reduction in Eh or pH (to pH = 7), releasing both dissolved iron and dissolved arsenic, is consistent with this diagram. For the observed arsenate/arsenite ratio of near unity at pH = 7, an Eh value of .016 is indicated. The stability boundary for ferrous ion/ferric hydroxide is given at .012 volts for a total ferrous iron concentration of 10^{-5} mole $liter^{-1}$, and -.047 volts for the ferrous iron concentration of 10^{-4} moles $liter^{-1}$. Within the context of analytical precision for quantitative arsenic speciation and total ferrous iron, this thermodynamic derived diagram is consistent with observed conditions.

The natural accumulation and concentration of arsenic through adsorption to ferric hydroxide would occur at slightly higher Eh-pH conditions than are now existing in the aquifer of study. Total dissolved arsenic, under these conditions, is controlled through adsorption, with arsenic V following a Langmuir isotherm and arsenic III adsorbed linearly with respect to concentration. Adsorption and retention of arsenic is subject to the stability of the adsorbate, ferric hydroxide. This adsorbate, when subject to a change toward reducing and/or acid conditions, is de-stabilized. Both arsenic III, arsenic V and iron (II) enter the solution phase as the ferric hydroxide dissolves.

If this proposed model for the control of arsenic by an adsorption equilibrium with ferric hydroxides is occurring within the study area, then a correlation should exist between the concentration of total dissolved arsenic and ferrous iron. Ferrous iron concentrations were determined for thirteen wells. These wells were selected because they represent the full range of arsenic concentration levels within the study area. Values for ferrous iron ranged from 0.106 mgl^{-1} to 7.77 mg l^{-1} (Table 6). The relationship between ferrous iron and total arsenic is shown in Figure 17. The relationship is linear, with a slope of -11.1 ug/mg and a correlation coefficient of 0.923. This means that the ferric hydroxide has adsorbed 1% of its weight in arsenic, a value that is not unreasonable. The well at the Northwest Intermediate School, the well of maximum arsenic contamination (96 ug l^{-1}) in the study area, is also the well with the highest concentration of ferrous iron (7.77 mg/l). Iron concentrations in excess of 5.0 mg l^{-1} are rare in northeast Ohio aquifers (Ohio EPA files). The two wells containing minimum concentrations of total arsenic, 0 ug l^{-1} and 4.7 ug l^{-1}, contain minimum amounts of ferrous iron, 0.106 mg l^{-1} and 0.101 mg l^{-1} respectively.

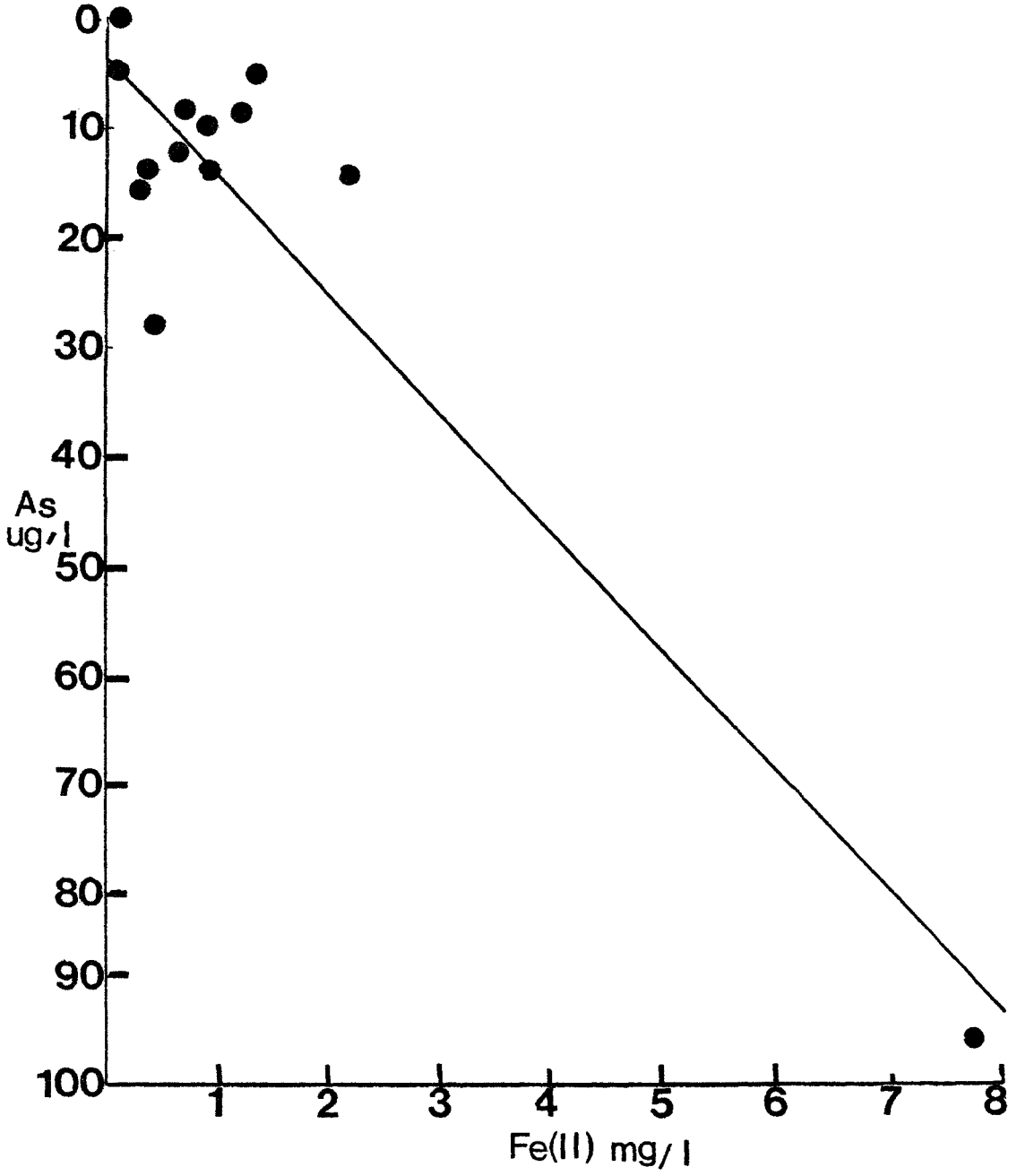

Figure 17. Relationship between ferrous iron and total arsenic for selected ground water samples.

Thus, the ferric hydroxide adsorption model is consistent with the data and suggests that the arsenic contamination is a natural phenomenon. The potential exists for this problem to occur elsewhere in Ohio. However, the specific conditions including redox, pH, mineralogy, and the necessary sequence of changes within the hydrogeochemical system that produced this contamination, is not likely to be repeated on a wide scale. Continued attention should be given to arsenic within Ohio's Appalachian Plateau Region and in other states.

Naturally occurring high levels of arsenic in ground water do not represent the only source of arsenic in drinking water. We have found (Strain et al., 1980) that the arsenic content in household drinking waters is elevated above the EPA limit of 50 ppb in more than one half of the samples and can be as high as 1600 ppb. The corrosive action of water on the metallic components of the plumbing system apparently leads to the elevated arsenic contents. Flushing the household system of standing water before use should reduce the arsenic, lead, and other toxic metal concentrations in the drinking water.

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APPENDIX

Sampling Stations

Station	Name	Address or Location
1	Abandoned Coal Mine, Drainage	NE 1/4, NE 1/4 sec. 25 Chippewa Township, Wayne County
2	Northwest Intermediate School	Erie St. Campus, Stark Co.
3	Northwest Intermediate School	Erie St. Campus, Stark Co.
4	Northwest High School	Erie St. Campus, Stark Co.
5	R. Yourichin	
6	Surface water: Swamp A	NE 1/4, NE 1/4 sec. 5, Lawrence Township, Stark County
7	Northwest Elementary School	Erie St. Campus, Stark Co.
8	G. Hoffman	882 Indian Hill Circle, Stark Co.
9	E. Kirkendall	884 W. Nimisila Rd., Summit Co.
10	R. Weigand	8896 Indian Hill Circle, Stark Co.
11	M. Hood	8968 Shoemaker Drive, Stark Co.
12	D. Nichols	8860 Shoemaker Drive, Stark Co.
14	Residence	6000 feet south of Clinton Landfill, Stark Co.
15	D. Chase	8252 Cleveland-Massillon Rd., Summit Co.
16	H. Munroe	Cottage 17-A, Luna Lake, Summit Co.
17	E. Baier	2534 W. Comet Road, Summit Co.
18	L. Schelcher	2285 W. Comet Road, Summit Co.
19	B. Witte	7500 Kepler Road, Summit Co.
20	J. Campbell	8127 Cleveland-Massillon Rd., Summit Co.
21	U.S. Post Office	Clinton, Summit Co.
22	C. Vasiloff	1470 W. Comet Road, Summit Co.
23	D. Sudimak	1440 W. Comet Road, Summit Co.
24	B. Rea	1544 W. Comet Road, Summit Co.
25	J. Zabadah	8805 Lever Road, Stark Co.

Station	Name	Address or Location
26	B. Chapman	8811 Lever Road, Stark Co.
26A	R. Gregg	8131 Lever Road, Stark Co.
27	J. Sparks	8277 Lever Road, Stark Co.
28	P. Cox	8561 Manchester, Summit Co.
29	C. Light	8500 Babst Avenue, Stark Co.
30	D. Johnson	861 Dunning Road, Stark Co.
31	P. Lewis	6739 Hampshire Road, Summit Co.
32	D. Koehler	1419 W. Nimisila Road, Summit Co.
33	D. Snyder	6823 Kepler, Summit Co.
34	R. Whitehead	6750 Kepler, Summit Co.
35	B. Gwyn	1730 Rheam Road, Summit Co.
36	J. Overholt	6341 Redbird Terrace, Summit Co.
37	R. Teaman	6296 Redbird Terrace, Summit Co.
38	Nimisila School Annex	6075 Manchester Road, Summit Co.
39	Franklin Township Fire Dept.	5605 Manchester Road, Summit Co.
40	D. Sandmann	5756 Fairview, Summit Co.
41	J. Henderson	1837 Limbach Road, Summit Co.
42	Residence	1833 Limbach Road, Summit Co.
43	Johns Road Discharge	NE 1/4, SW 1/4 sec. 15, Franklin Twp., Summit Co.
44	R. Glover	5575 Swanson Road, Summit Co.
45	O. Rieder	5166 Donner Drive, Summit Co.
50	Chapel Hill Home	NE 1/4, NE 1/4 Sec. 10, Lawrence Twp., Stark Co.
51	Canal Castings	816 Milan Street, Stark Co.
52	Wadsworth Machine Co.	13786 Warwick Road, Stark Co.
53	N. Podnar	14580 Warwick Road, Stark Co.

Station	Name	Address or Location
54	W. Wagner	15101 Warwick Road, Stark Co.
55	T. Faye	8073 Canal Fulton Road, Summit Co.
56	Residence	8543 Erie Avenue, Stark Co.
57	L. Gandee	8235 Erie Avenue, Stark Co.
58	P. MacGregor	8955 Kepler Road, Stark Co.
59	H. Fetherolf	8744 Kepler Road, Stark Co.
60	E. Neidert	8622 Kepler Road, Stark Co.
61	C. Witherow	8775 Kepler Road, Stark Co.
62	J. Johnson	8590 Kepler Road, Stark Co.
63	G. Johnson	8550 Kepler Road, Stark Co.
64	L. Johnson	8484 Kepler Road, Stark Co.
65	L. Podnar	8441 Kepler Road, Stark Co.
66	G. Kiser	8409 Kepler Road, Stark Co.
67	K. Youngblood	8384 Erie Avenue, Stark Co.
68	Stream	NE 1/4, SW 1/4 Sec. 4 Lawrence Twp., Start Co.
69	D. Minard	8615 Erie Avenue, Stark Co.
70	Clinton Amoco	7783 Main Street, Summit Co.
71	Canal Fulton, Municipal Well No. 6	NE 1/4, NE 1/4 Sec. 9 Lawrence Twp., Stark Co.
72	Canal Fulton, Municipal Well No. 5	NE 1/4, NE 1/4 Sec. 9 Lawrence Twp., Stark Co.
73	Canal Fulton, Municipal Well No. 4	NE 1/4, NE 1/4 Sec. 9 Lawrence Twp., Stark Co.
74	R. Kempe	8059 Lever Road, Stark Co.
75	Residence	8460 Lever Road, Stark Co.
76	J. McGrew	8272 Lever Road, Stark Co.
77	H. Ries	11845 Portage Road, Stark Co.

Station	Name	Address or Location
78	R. Ries	11845 Portage Road, Stark Co.
79	D. Rogers	11335 Lafayette Drive, Stark Co.
80	Canal Fulton Baptist Church	NE 1/4, SE 1/4 Sec. 14 Lawrence Twp., Stark Co.
81	Surface Runoff	SW 1/4, NW 1/4 Sec. 4 Lawrence Twp., Stark Co.
82	Surface Seepage	SW 1/4, NW 1/4 Sec. 4 Lawrence Twp., Stark Co.
83	G. Miller	19102 Galehouse Road, Wayne Co.
84	D. Graves	7652 4th Street, Clinton, Summit Co.
85	E. Fox	18779 Galehouse Road, Wayne Co.
86	E. Browning	18386 Galehouse Road, Wayne Co.
87	S. Knicely	11439 Fraze Road, Wayne Co.
88	D. Roberts	11641 Fraze Road, Wayne Co.
89	B. Wilkinson	11865 Fraze Road, Wayne Co.
90	R. Pierce	11778 Clinton Road, Wayne Co.
91	P. Simons	8304 Kepler Road, Stark Co.
92	H. Johnson	8841 Kepler Road, Stark Co.
93	D. Traxler	8174 Erie Avenue, Stark Co.
94	Surface Water Flow	SE 1/4, NW 1/4 Sec. 4 Lawrence Twp., Stark Co.